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SELECTED METAL-NONMET..(U) THERMOPHYSICAL AND  
ELECTRONIC PROPERTIES. INFORMATION ANALYSIS..  
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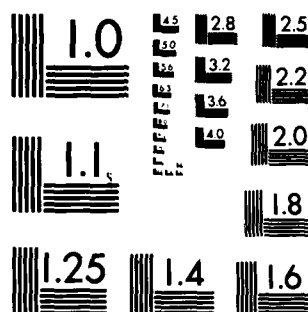
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THERMOPHYSICAL, ELECTRICAL, AND OPTICAL PROPERTIES OF  
SELECTED METAL-NONMETAL TRANSITION MATERIALS

Comprehensive Bibliography With Typical Data

Y. S. TOULOUKIAN, C. Y. HO, and J. F. CHANEY

CINDAS REPORT 50

February 1978

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report presents a comprehensive bibliography on twelve thermophysical, electrical, and optical properties of twelve selected priority metal-nonmetal transition materials. Typical data on each property of each of the twelve materials are provided, if available. The nature of the metal-nonmetal transitions in the twelve materials and their transition temperatures and pressures are summarized.		

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West Lafayette, Indiana 47906

## PREFACE

This final report was prepared by the Thermophysical and Electronic Properties Information Analysis Center (TEPIAC), a DoD Information Analysis Center operated by the Center for Information and Numerical Data Analysis and Synthesis (CINDAS), Purdue University, West Lafayette, Indiana, under Contract No. DSA900-77-C-3758 with the Defense Logistics Agency (DLA), Alexandria, Virginia, with Mr. J. L. Blue (Hq. DLA) as the IAC Program Manager and Mr. Samuel Valencia (Army Materials and Mechanics Research Center) as the Contracting Officer's Technical Representative.

This report contains the results of Phases II and III of the task assigned to TEPIAC for the third year (1977) of the program conducted for the Tri-Service Laser Hardened Materials and Structures Subpanel of the High Energy Laser Review Group. The results of Phase I of the task have already been reported.

The work for Phase II of the task for 1977 was to search the world literature and to prepare a complete bibliography on seven thermophysical, electrical, and optical properties of twelve selected priority metal-nonmetal transition materials, and the work for Phase III was to provide typical data on each property of each of the twelve materials. Not only all these have been accomplished, but a much wider scope of coverage of the work has been achieved. In addition to the seven properties required, results on four extra properties (thermal emittance, reflectance, absorptance, and transmittance), which are not required by the task assignment but are believed by TEPIAC to be important for the selected materials, are also included, and the results on optical properties have been divided for reporting separately on absorption coefficient and on refractive index so as to give more specific information. Consequently, bibliographic information and data for twelve thermophysical, electrical, and optical properties are presented in this report instead of for seven properties as required. Furthermore, research documents on the characteristics of the selected materials and on the nature of their metal-nonmetal transitions have been thoroughly reviewed and studied, and the resulting information is also reported herein additionally. This information will certainly enhance greatly the usefulness of the report. Therefore, the accomplishments of TEPIAC in this task have far exceeded the requirements.

The work for Phase I of the task for 1977 produced a complete listing of potential metal-insulator transition materials, which were reported in the following categories:

- (1) Transition-metal chalcogenides (binary)
- (2) Mixed transition-metal chalcogenides
- (3) Rare-earth chalcogenides
- (4) Mixed rare-earth chalcogenides
- (5) Other binary chalcogenides
- (6) Mixed chalcogenides (not oxides)
- (7) Mixed oxides (glasses)
- (8) Multiple chalcogenides
- (9) Chalcogenide alloys and other alloys
- (10) Ovshinsky glasses and related materials
- (11) Binary halides
- (12) Elements
- (13) Metal-ammonia solutions
- (14) Rare gas-metal systems; metal/inert element
- (15) Organic materials
- (16) Miscellaneous materials.

The above classes of materials represented 58 sub-groups of materials and 128 individual materials.

The task assigned to TEPIAC for the first year (1975) of the program resulted in the publication of a 1058-page volume entitled "Thermophysical Properties of Selected Aerospace Materials. Part I: Thermal Radiative Properties," while that for the second year (1976) resulted in a 242-page volume entitled "Thermophysical Properties of Selected Aerospace Materials. Part II: Thermophysical Properties of Seven Materials."

February 1978  
West Lafayette, IN 47906

Y. S. TOULOUKIAN  
Director of CINDAS  
Distinguished Atkins Professor  
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Purdue University

## SUMMARY

This report presents a comprehensive bibliography on twelve thermophysical, electrical, and optical properties of twelve selected priority metal-nonmetal transition materials. Typical data on each property of each of the twelve materials are provided, if available.

The nature of the metal-nonmetal transitions in the twelve materials and their transition temperatures and pressures are summarized in the following table.

Nature of Transitions and Transition Temperatures and Pressures

Material	Transition Temp. (K)	Nature of Transition
$\text{VO}_2$	341	Semiconducting-metallic Diamagnetic-paramagnetic Monoclinic-tetragonal
$\text{V}_2\text{O}_3$	150-173	Semiconducting-metallic Antiferromagnetic-paramagnetic Monoclinic-rhombohedral
	350-550	Metallic-poorer metallic
$(\text{Cr}_x\text{V}_{1-x})_2\text{O}_3$	150-173	Semiconducting-metallic Antiferromagnetic-paramagnetic Monoclinic-rhombohedral
	250-400 ( $0.005 \leq x \leq 0.018$ )	Rhombohedral ( $\alpha$ -corundum)- rhombohedral ( $\beta$ -corundum)
$(\text{Ti}_x\text{V}_{1-x})_2\text{O}_3$	0-173 ( $0.051 \geq x \geq 0$ )	Semiconducting-metallic Antiferromagnetic-paramagnetic Monoclinic-rhombohedral
$\text{V}_3\text{O}_5$	425	Change in monoclinic lattice parameters and in cell volume
$\text{Ti}_2\text{O}_3$	400-550	Semiconducting-metallic Change in rhombohedral lattice parameters Crossing of two electron energy bands
$\text{NbO}_2$	1070	Semiconducting-metallic Softening of vibrational modes
	Room temp. under applied electric field	Switching from high to low electrical resistance under an applied electric field
$\text{EuO}$	69.29	Ferromagnetic-paramagnetic
	Room temp. under high pressure	Insulating-metallic and change in cubic lattice parameter under a high pres- sure ( $p > 300 \text{ kb}$ )



v

Nature of Transitions and Transition Temperatures and Pressures (Continued)

Material	Transition Temp. (K)	Nature of Transition
$\text{Eu}_{1+x}\text{O}_{1-x}$	50	Metallic-semiconducting
	69.29	Ferromagnetic-paramagnetic
$\text{Na}_x\text{WO}_3$	390-440	Anomalies in properties
NiS	623	Rhombohedral ( $\alpha$ -NiS)-hexagonal ( $\beta$ -NiS)
$\beta$ -NiS	260-280	Semiconducting-metallic Antiferromagnetic-paramagnetic
$\text{NiS}_2$	40	Antiferromagnetic-paramagnetic
	Room temp. under high pressure	Insulating-metallic under a high pressure of 32 kb at increasing pressure and of 8 kb at decreasing pressure
SmS	Room temp. under high pressure	Semiconducting-metallic under a high pressure of 6.5 kb at increasing pressure and of 0.8 kb at decreasing pressure

The numbers of references on the twelve properties of the twelve materials uncovered through the systematic and exhaustive search of the world literature are summarized in the table which appears on the next page.

Number of References Available on Twelve Properties of Twelve Materials

Material	Thermal Conductivity	Specific Heat	Thermal Expansion	Thermal Diffusivity	Thermal Emissance	Thermal Reflectance	Thermal Absorbance	Thermal Transmittance	Electrical Resistivity	Dielectric Constant	Absorption Coefficient	Refractive Index
VO <sub>2</sub>	1	7	11	0	0	18	2	9	159	7	11	8
V <sub>2</sub> O <sub>3</sub>	0	12	5	0	2	8	1	3	84	4	4	2
(Cr <sub>x</sub> V <sub>1-x</sub> ) <sub>2</sub> O <sub>3</sub>	0	6	2	0	0	1	0	0	17	1	1	1
(Ti <sub>x</sub> V <sub>1-x</sub> ) <sub>2</sub> O <sub>3</sub>	0	3	1	0	0	0	0	0	11	0	0	0
V <sub>3</sub> O <sub>5</sub>	0	2	1	0	0	1	0	0	19	0	0	1
Ti <sub>2</sub> O <sub>3</sub>	1	23	5	0	0	4	1	1	46	4	0	0
NbO <sub>2</sub>	0	10	1	0	0	0	0	0	16	1	0	0
EuO	10	23	2	1	0	16	0	7	53	10	28	3
Na <sub>x</sub> WO <sub>3</sub>	4	7	1	0	0	8	2	0	25	2	1	1
NiS	1	8	3	0	0	1	0	0	34	1	0	0
NiS <sub>2</sub>	0	2	3	0	0	2	0	0	16	0	0	0
SmS	3	5	1	0	0	17	6	3	43	1	7	0

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## 1. INTRODUCTION

This report presents a comprehensive bibliography that has been prepared through a systematic and exhaustive search of the world literature for pertinent references on twelve thermophysical, electrical, and optical properties of twelve selected priority metal-nonmetal transition materials. Typical data on each property of each of the twelve materials are provided, if available.

The twelve properties covered are:

- (1) Thermal conductivity
- (2) Specific heat
- (3) Thermal linear expansion
- (4) Thermal diffusivity
- (5) Thermal emittance
- (6) Thermal reflectance
- (7) Thermal absorptance
- (8) Thermal transmittance
- (9) Electrical resistivity
- (10) Dielectric constant
- (11) Absorption coefficient
- (12) Refractive index.

The twelve selected metal-nonmetal transition materials are:

- (1) Vanadium dioxide ( $\text{VO}_2$ )
- (2) Vanadium sesquioxide ( $\text{V}_2\text{O}_3$ )
- (3) Vanadium sesquioxide doped with chromium
- (4) Vanadium sesquioxide doped with titanium
- (5) Trivanadium pentoxide ( $\text{V}_3\text{O}_5$ )
- (6) Titanium sesquioxide ( $\text{Ti}_2\text{O}_3$ )
- (7) Niobium dioxide ( $\text{NbO}_2$ )
- (8) Europium monoxide ( $\text{EuO}$ )
- (9) Sodium tungsten bronze ( $\text{Na}_x\text{WO}_3$ )
- (10) Nickel monosulfide ( $\text{NiS}$ )
- (11) Nickel disulfide ( $\text{NiS}_2$ )
- (12) Samarium monosulfide ( $\text{SmS}$ ).

A list of pertinent reference numbers and the typical data on each property of each material are presented in each subsection of Section 2. Research documents on the characteristics of the selected materials and on the nature of the metal-nonmetal transition in each of the materials have been thoroughly reviewed and studied and the resulting information is given at the beginning of each of the subsections. This information is believed valuable and will greatly enhance the usefulness of this report.

The complete bibliographic citations for the 678 references are given in Section 3. The references are listed in three separate groups: the first group with reference numbers prefixed with the letter T, the second group with reference numbers prefixed with the letter E, and the third group with reference numbers prefixed with the letter A.

The information on the nature of the metal-nonmetal transition in the selected materials and their transition temperatures and pressures is summarized and presented in the SUMMARY, in which statistics on the number of references available for each property of each material is also given.

## 2. THERMOPHYSICAL, ELECTRICAL, AND OPTICAL PROPERTIES OF SELECTED METAL-NONMETAL TRANSITION MATERIALS

### 2.1. Vanadium Dioxide

Vanadium dioxide ( $\text{VO}_2$ ) forms deep-blue crystals which, above 341 K, have a tetragonal crystal structure with a density of  $4.66 \text{ g cm}^{-3}$ . It is a metal with relatively low mobility charge carriers above the transition temperature (341 K). The transition temperature may be lowered by raising the pressure. Vanadium dioxide melts at about 1910 K and decomposes at about 3300 K.

Below 341 K vanadium dioxide is a semiconductor and has a monoclinic crystal structure with a density of  $4.65 \text{ g cm}^{-3}$ . The chains of octahedra within the crystals are puckered below the transition temperature and the metal atoms are shifted so as to form V-V pairs within the chains. The bonding within these chains is cooperative, the d-electrons on each metal atom being trapped into localized V-V bonds so as to quench the metallic conductivity along the c-axis. For high quality crystals the metal-semiconductor transition is extremely sharp and electrical resistivity changes of up to 6 orders of magnitude have been observed at the transition temperature, at which there is also an accompanying paramagnetic to diamagnetic transition as the magnetic moment drops dramatically.

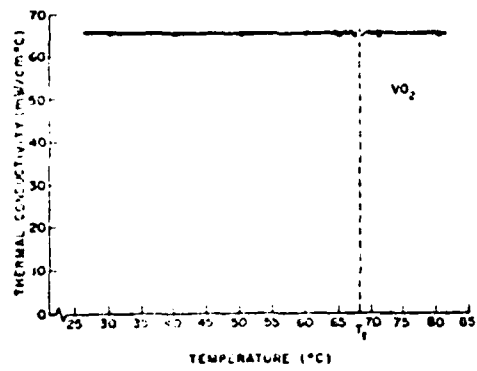
The cause of the transition from a semiconducting to a metallic state (with increasing temperature) that is associated with a change from a lower to a higher symmetry crystal structure has been explained by using a mechanism proposed by N. F. Mott. According to Mott's theory, the transition is explained as a discontinuous change from a state of bound electrons to a state of delocalized collective electrons as the electron density exceeds a critical value.

A systematic and exhaustive search of the world literature for the pertinent references on the thermophysical, electrical, and optical properties of vanadium dioxide has been conducted and the results are given in the following subsections. Typical data on each of the properties are also presented, if available.

#### a. Thermal Conductivity

The literature search uncovers the following reference: T051827.

Typical data on the thermal conductivity of vanadium dioxide as taken from T051827 are shown below.



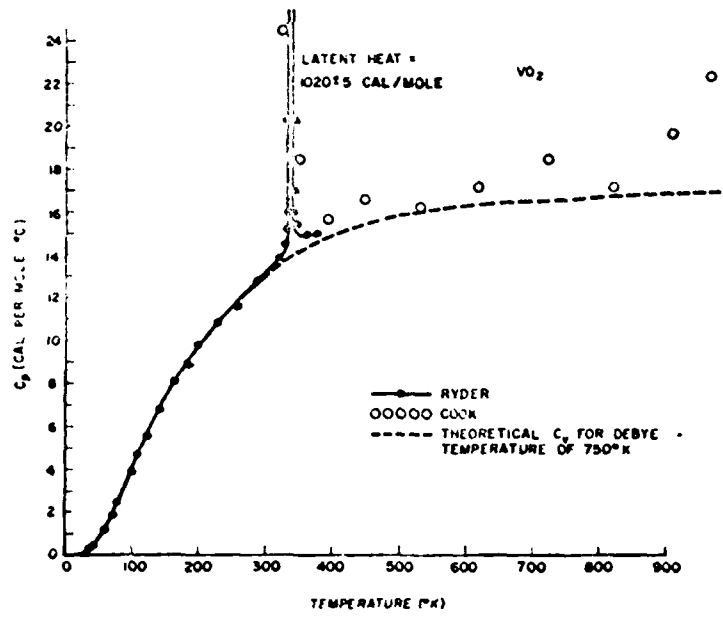
Thermal conductivity of a typical sample of VO<sub>2</sub>.

b. Specific Heat

The literature search uncovers the following references:

T007006	T051827	T074700	T088479
T049274	T070838	T085437	

Typical data on the specific heat of vanadium dioxide as taken from T051827 are shown below.



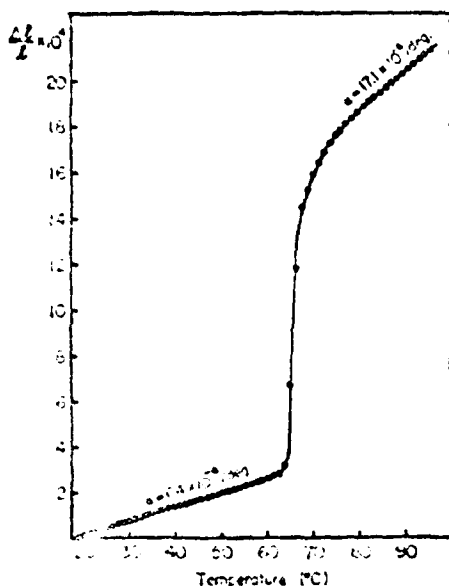
Heat capacity of VO<sub>2</sub>.

### c. Thermal Linear Expansion

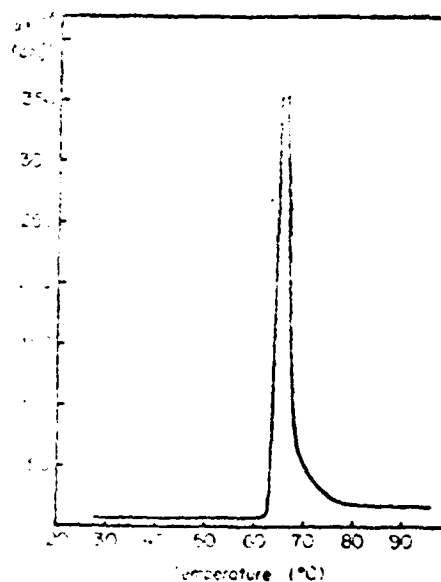
The literature search uncovers the following references:

T046134	T060200	T072937	E015066
T052868	T065581	T074517	A000078
T053775	T065924	T074700	

Typical data on the thermal linear expansion of vanadium dioxide as taken from E015066 are shown below.



Thermal dilatation vs. temperature.



Thermal expansion coefficient vs. temperature.

### d. Thermal Diffusivity

The literature search uncovers no reference on the thermal diffusivity.

### e. Thermal Emittance

The literature search uncovers no reference on the thermal emittance.

### f. Thermal Reflectance

The literature search uncovers the following references:

T039935	T051781	T061280	T065761
T049963	T054691	T065719	T065989



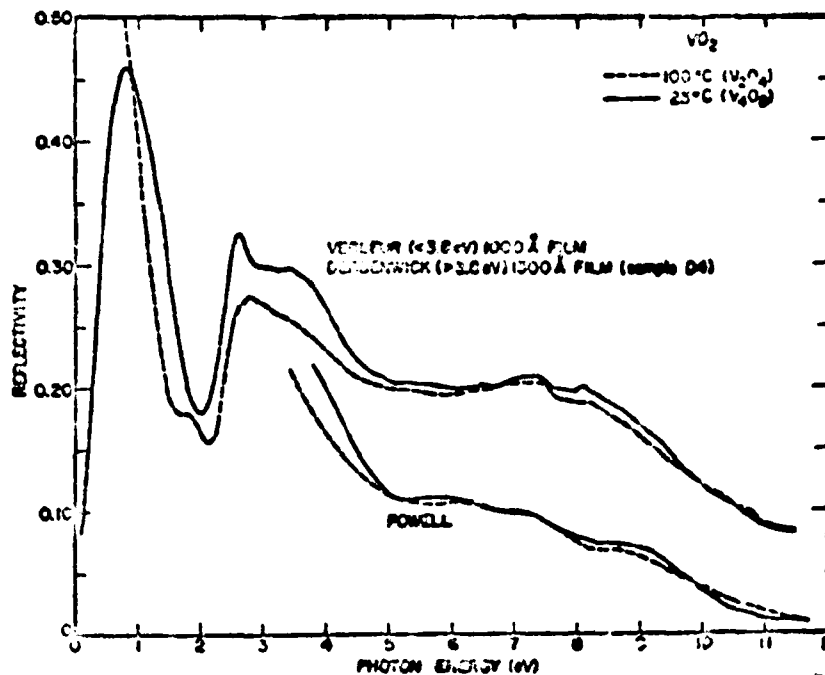
T077679  
T086795  
T087580

E032001  
E047476  
E053110

A000079  
A000080  
A000081

A000082

Typical data on the reflectance of vanadium dioxide as taken from T065761 are shown below.



Reflectivity of VO<sub>2</sub> above and below the transition temperature for  $0.1 \leq h\nu \leq 11.5$  eV. The data of Powell were taken on a thin film sample.

#### g. Thermal Absorptance

The literature search uncovers the following references: A000083 and A000084. However, copies of these documents are not available at this time for giving typical data.

#### h. Thermal Transmittance

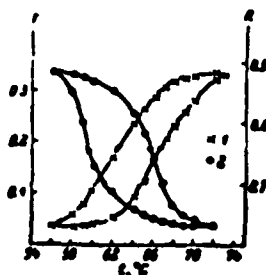
The literature search uncovers the following references:

T049963  
T054069  
T082265

T082399  
T086795  
T087395

T087580  
T087819  
E053110

Typical data on the transmittance of vanadium dioxide as taken from T087580 are shown below.



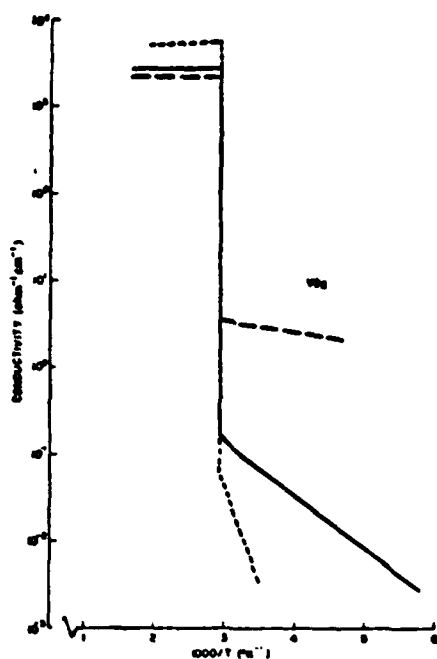
Temperature dependences of the reflection (1) and transmission (2) coefficients of  $\text{VO}_2$  films at  $\lambda = 2.2$  mm.

### 1. Electrical Resistivity

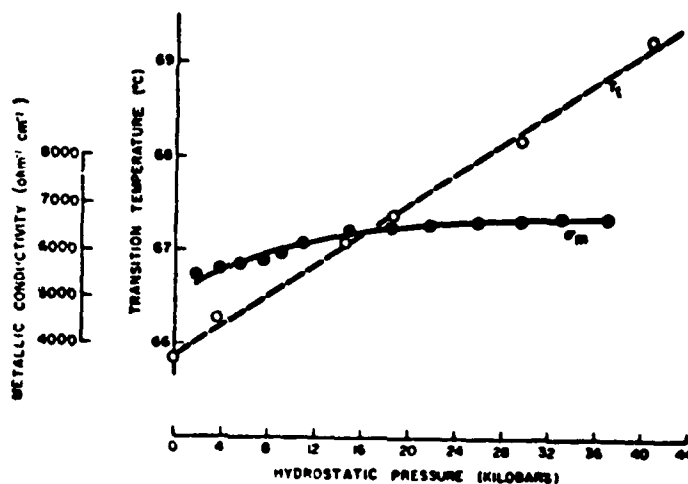
The literature search uncovers the following references:

T049963	E028053	E042028	E053261	E078332	E103176	A000095	A000115
T051827	E028056	E042400	E053271	E079687	E103573	A000096	A000116
T065831	E028295	E042472	E054556	E082690	E103872	A000097	A000117
T065989	E028522	E043005	E055974	E084145	E104764	A000098	A000118
T072883	E028824	E044791	E056765	E085575	E104938	A000099	A000119
T082265	E029315	E045085	E056946	E087776	E105110	A000100	A000120
T085437	E029436	E045093	E057718	E088213	A000031	A000101	A000121
T087580	E032357	E045947	E058639	E088981	A000032	A000102	A000122
T087819	E032361	E046365	E060610	E090433	A000081	A000103	A000123
T088479	E033339	E046405	E060740	E091130	A000082	A000104	A000124
E003081	E034169	E047247	E064843	E092143	A000085	A000105	A000125
E003739	E034673	E047249	E066369	E093158	A000086	A000106	A000126
E012182	E034752	E047476	E068739	E093516	A000087	A000107	A000127
E015066	E037145	E047834	E069102	E093696	A000088	A000108	A000128
E017395	E038392	E048788	E073819	E096635	A000089	A000109	A000129
E019012	E039259	E048961	E073965	E096855	A000090	A000110	A000130
E023136	E039349	E049283	E074009	E100055	A000091	A000111	A000131
E024796	E039364	E049398	E077111	E100056	A000092	A000112	A000132
E027129	E039973	E053110	E077608	E100757	A000093	A000113	A000133
E027846	E041464	E053113	E078207	E101229	A000094	A000114	

Typical data on the electrical resistivity of vanadium dioxide as taken from T051827 are shown below.



Temperature dependence of the conductivity of three typical samples of  $\text{VO}_2$ .



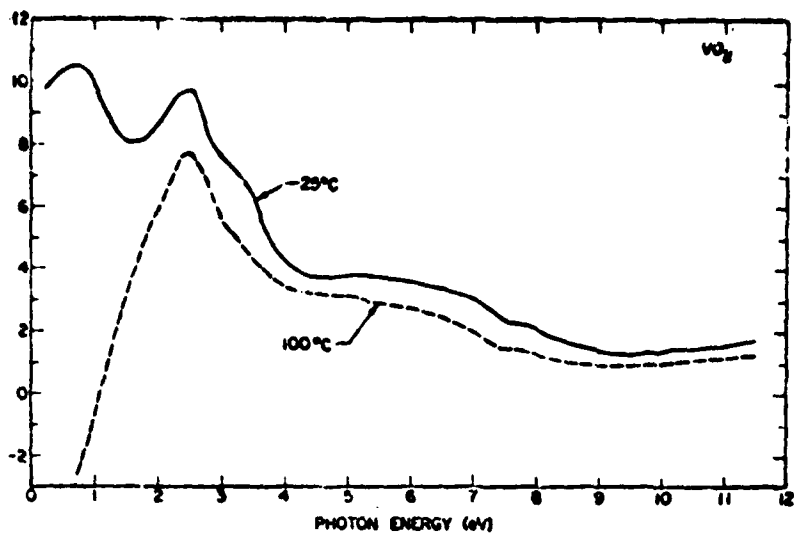
Hydrostatic pressure dependence of the transition temperature and metallic conductivity in  $\text{VO}_2$ .

#### j. Dielectric Constant

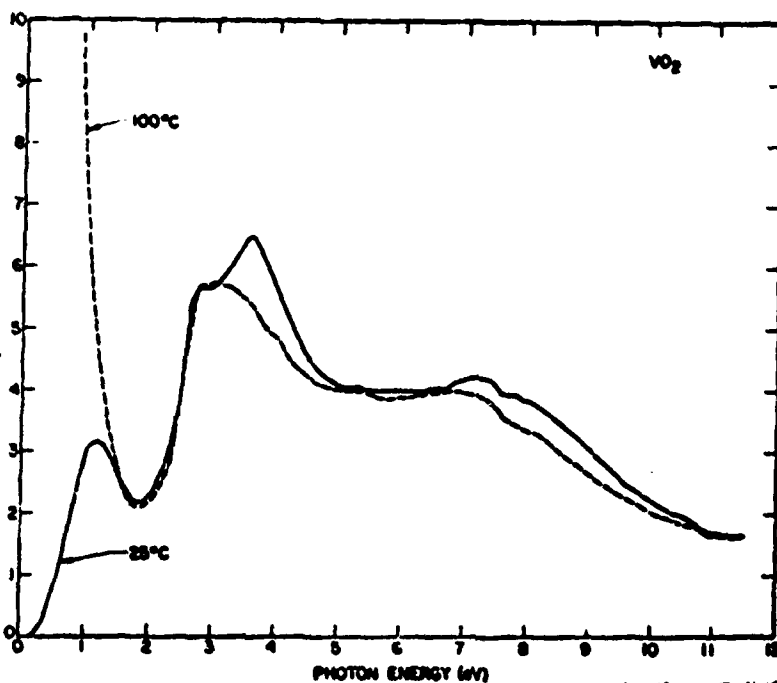
The literature search uncovers the following references:

T049963	T087580	E053110	E096832
T065989	T089279	E087881	

Typical data on the dielectric constant of vanadium dioxide as taken from T065761 are shown below.



Real part of the  $\text{VO}_2$  complex relative dielectric constant  
(Determined from the reflectance spectrum).



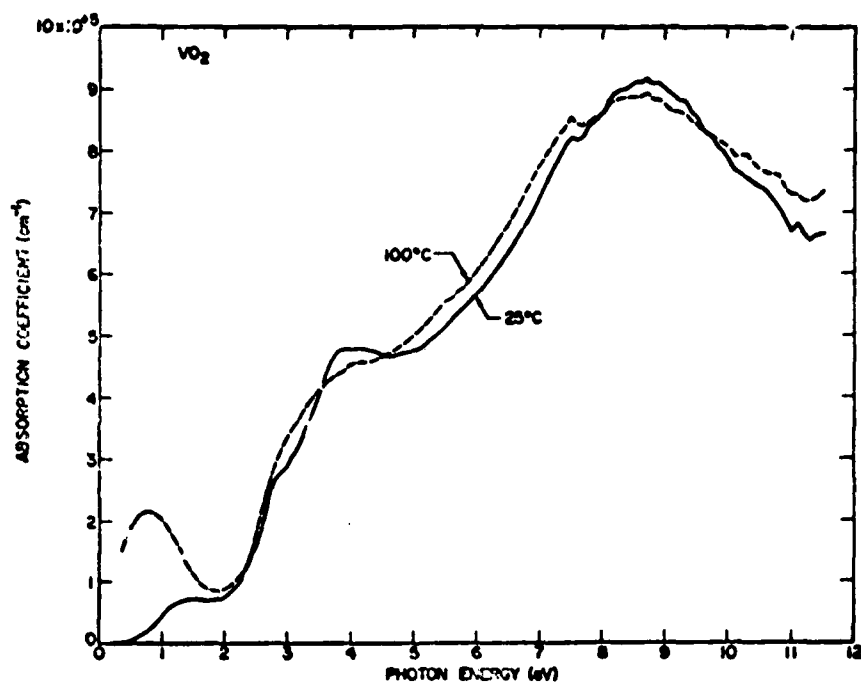
Imaginary part of the  $\text{VO}_2$  complex relative dielectric constant  
(Determined from the reflectance spectrum).

### k. Absorption Coefficient

The literature search uncovers the following references:

T049482	T065989	T087819	E053110
T049963	T077679	T089687	A000127
T065761	T087580	E045947	

Typical data on the absorption coefficient of vanadium dioxide as taken from T065761 are shown below.



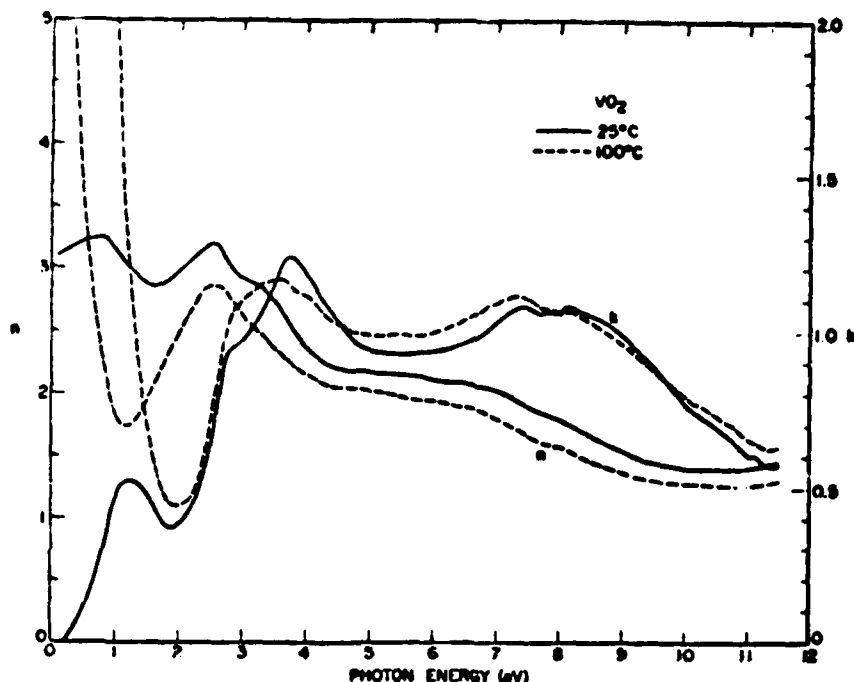
Optical absorption coefficient of VO<sub>2</sub> (Determined from the reflectance spectrum).

### 1. Refractive Index

The literature search uncovers the following references:

T049482	T065989	T087580	E053110
T065761	T077679	E045947	A000127

Typical data on the refractive index of vanadium dioxide as taken from T065761 are shown below.



Real and imaginary parts of the  $\text{VO}_2$  complex refractive index  
(Determined from the reflectance spectrum).

## 2.2. Vanadium Sesquioxide

Vanadium sesquioxide ( $\text{V}_2\text{O}_3$ ) is a gray-black paramagnetic metallic crystal with a rhombohedral (hexagonal) crystal structure at temperatures above approximately 160 K, below which it is an antiferromagnetic semiconductor with a monoclinic crystal structure. The transition temperature has been reported to be 150 to 173 K and may be lowered by raising the pressure. The transition is associated with a sudden change of about  $10^6$  times in the electrical resistivity within a single degree change of temperature. Vanadium sesquioxide melts at 2243 K and decomposes at about 3300 K. Its density is  $4.87 \text{ g cm}^{-3}$  at room temperature. It possesses only a narrow range of homogeneity and is oxidized in air to become dioxide.

As for vanadium dioxide, the semiconductor-to-metal transition of vanadium sesquioxide, which is accompanied also by a crystallographic transition and a magnetic transition, has been explained similarly by the Mott's theory. The fact that vanadium sesquioxide is the only one of a series of vanadium oxides that has antiferromagnetic ordering below the transition temperature is attributed to particular features of the crystal structure of this compound.

Anomalies in thermal, electrical, and other properties in the temperature range 350 to 550 K have also been observed. At this high-temperature transition, vanadium sesquioxide transforms from a metal to a poorer-conductivity metal.

A systematic and exhaustive search of the world literature for the pertinent references on the thermophysical, electrical, and optical properties of vanadium sesquioxide has been conducted and the results are given in the following subsections. Typical data on each of the properties are also presented, if available.

#### a. Thermal Conductivity

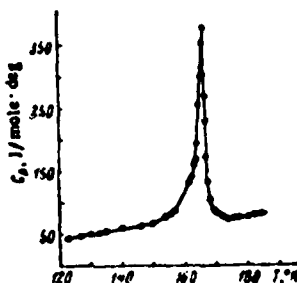
The literature search uncovers no reference on the thermal conductivity.

#### b. Specific Heat

The literature search uncovers the following references:

T059918	T070144	T085437	T088468
T060491	T070653	T087463	T088479
T069203	T077803	T087626	E086761

Typical data on the specific heat of vanadium sesquioxide as taken from T069203 are shown below.



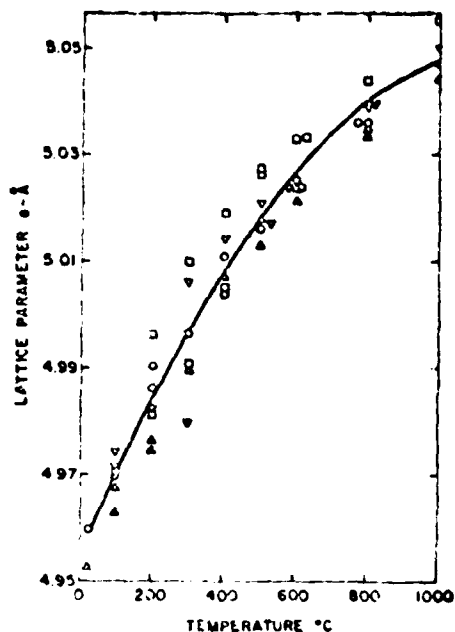
Anomaly in the heat capacity of  $V_2O_3$  in the region of the semiconductor-metal phase transition ( $T_C = 165.66$  K).

#### c. Thermal Linear Expansion

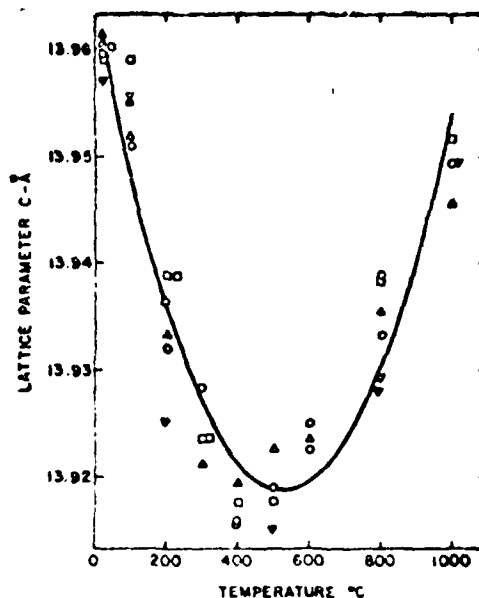
The literature search uncovers the following references:

T055571	T060489	T071059
T059918	T069622	

Typical data on the thermal linear expansion of vanadium sesquioxide as taken from T071059 are shown below.



a axis lattice parameter of corundum structure V<sub>2</sub>O<sub>3</sub>.



c axis lattice parameter of corundum structure V<sub>2</sub>O<sub>3</sub>.

#### Lattice parameters and expansion coefficients of V<sub>2</sub>O<sub>3</sub>.

25-200 °C	25-400 °C	400-1000 °C
$a = 4.951 + 1.619 \times 10^{-4}T - 6.905 \times 10^{-7}T^2 \text{ Å}$	$c = 13.965 - 1.77 \times 10^{-4}T + 1.257 \times 10^{-7}T^2 \text{ Å}$	$c = 13.905 + 1.575 \times 10^{-4}T + 2.69 \times 10^{-7}T^2 \text{ Å}$
$\alpha_a = 3.26 \times 10^{-5} - 2.871 \times 10^{-8}T + 7.747 \times 10^{-11}T^2 \text{ °C}^{-1}$	$\alpha_c = -1.273 \times 10^{-5} + 1.782 \times 10^{-8}T + 2.405 \times 10^{-11}T^2 \text{ °C}^{-1}$	$\alpha_c = 1.131 \times 10^{-5} + 3.88 \times 10^{-8}T - 2.22 \times 10^{-11}T^2 \text{ °C}^{-1}$
$c = 13.963 - 1.68 \times 10^{-4}T + 1.577 \times 10^{-7}T^2 \text{ Å}$		
$\alpha_c = -1.106 \times 10^{-5} + 2.258 \times 10^{-8}T + 1.049 \times 10^{-11}T^2 \text{ °C}^{-1}$		

#### d. Thermal Diffusivity

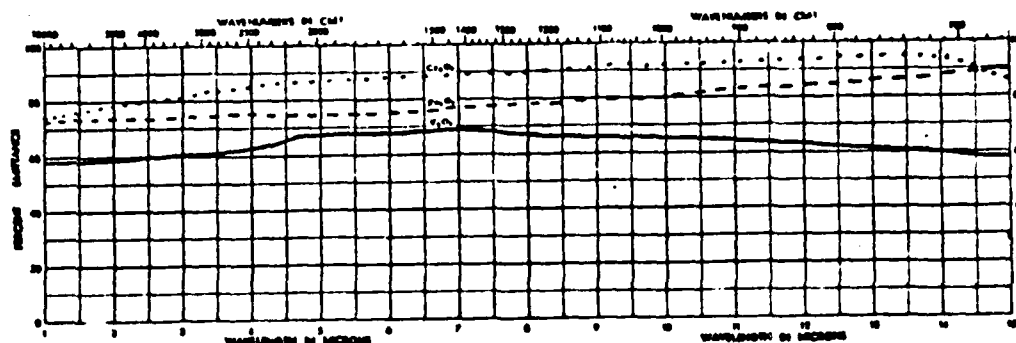
The literature search uncovers no reference on the thermal diffusivity.

#### e. Thermal Emittance

The literature search uncovers the following references: T022522 and T035907.



Typical data on the emittance of vanadium sesquioxide as taken from T035907 are shown below.



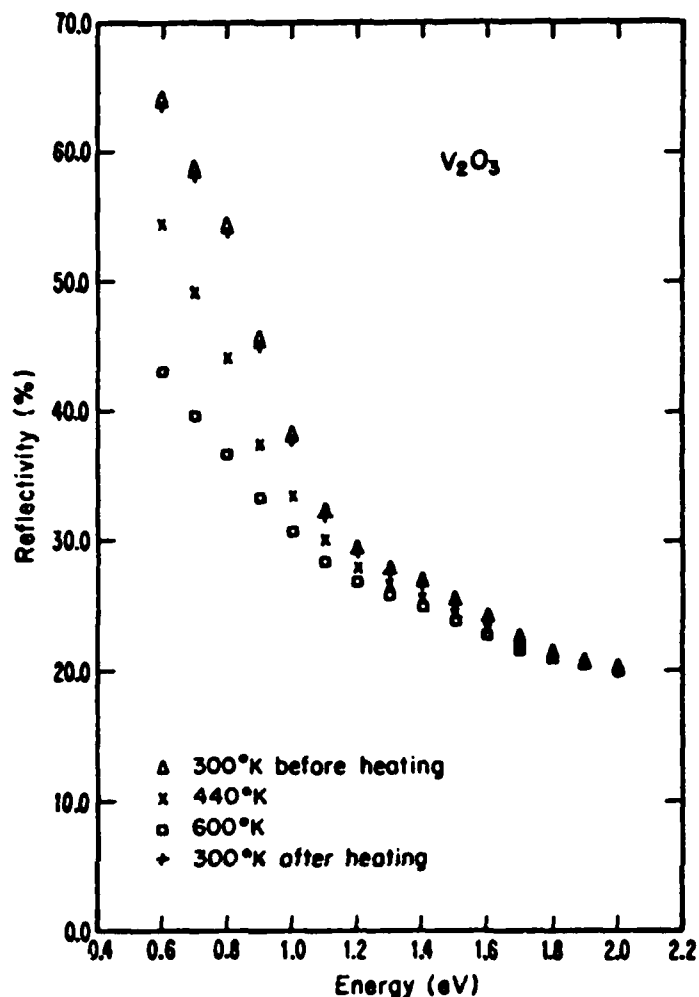
Emittance of  $V_2O_3$ ,  $Fe_3O_4$ , and  $Cr_2O_3$ .

#### f. Thermal Reflectance

The literature search uncovers the following references:

T062741	T067613	T080104	T089293
T065719	T067934	T087566	E053110

Typical data on the reflectance of vanadium sesquioxide as taken from E053110 are shown below.



The reflectivity of a  $V_2O_3$  crystal at different temperatures as a function of photon energy.

#### g. Thermal Absorptance

The literature search uncovers the following reference: A000134. However, a copy of this document is not available at this time for giving typical data. In addition, this document is an abstract of a study and may not contain any data.

#### h. Thermal Transmittance

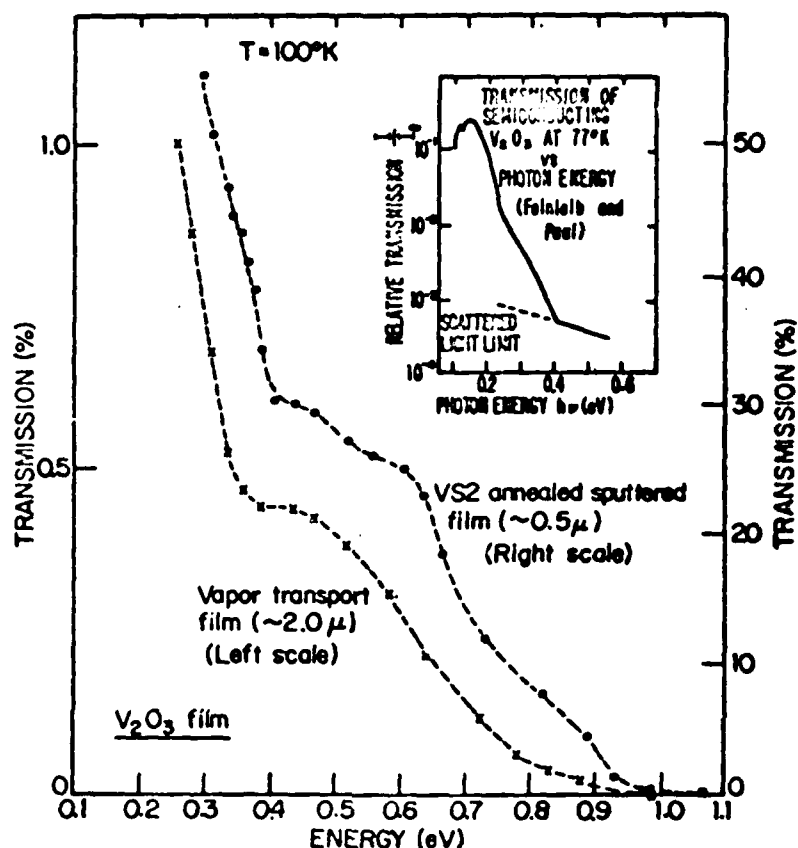
The literature search uncovers the following references:

T067613

T068160

E053110

Typical data on the transmittance of vanadium sesquioxide as taken from E053110 are shown below.



Low temperature transmission of a  $V_2O_3$  film grown by vapor transport and of an annealed  $V_2O_3$  sputtered film, compared with that of a single crystal measured by Feinleib and Paul.

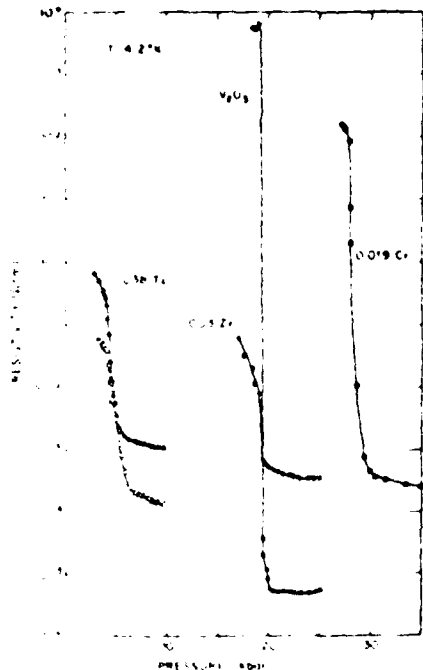
#### 1. Electrical Resistivity

The literature search uncovers the following references:

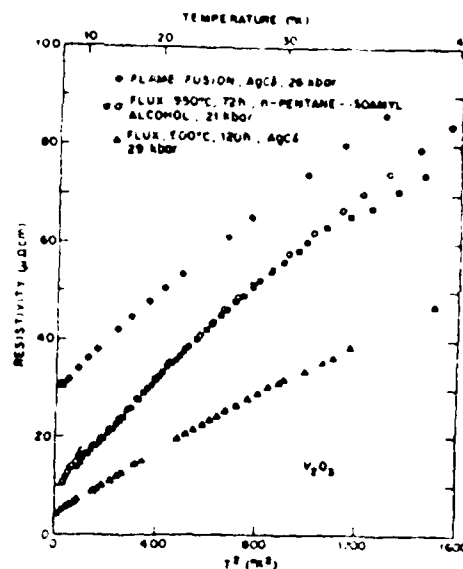
T069622	E004585	E012765	E023212	E035092	E043005	E051150
T077803	E004897	E012944	E024796	E037145	E045181	E053110
T085437	E006012	E013047	E027652	E038630	E046005	E053261
T088479	E009741	E014700	E028607	E039648	E047489	E053775
E003081	E010442	E015182	E029315	E039973	E048961	E053934
E003739	E012182	E019012	E032357	E042472	E049094	E056286

E057860	E086761	E104938	A000130	A000137	A000143	A000149
E063980	E088400	A000075	A000131	A000138	A000144	A000150
E064843	E091134	A000076	A000132	A000139	A000145	A000151
E066921	E093757	A000077	A000133	A000140	A000146	A000152
E082690	E095576	A000128	A000135	A000141	A000147	A000153
E084144	E096635	A000129	A000136	A000142	A000148	A000154

Typical data on the electrical resistivity of vanadium sesquioxide as taken from T069622 are shown below.



Electrical resistivity perpendicular to the c axis (closed symbols) vs. pressure at 4.2 K for doped  $V_2O_3$ . All curves are for decreasing pressure.



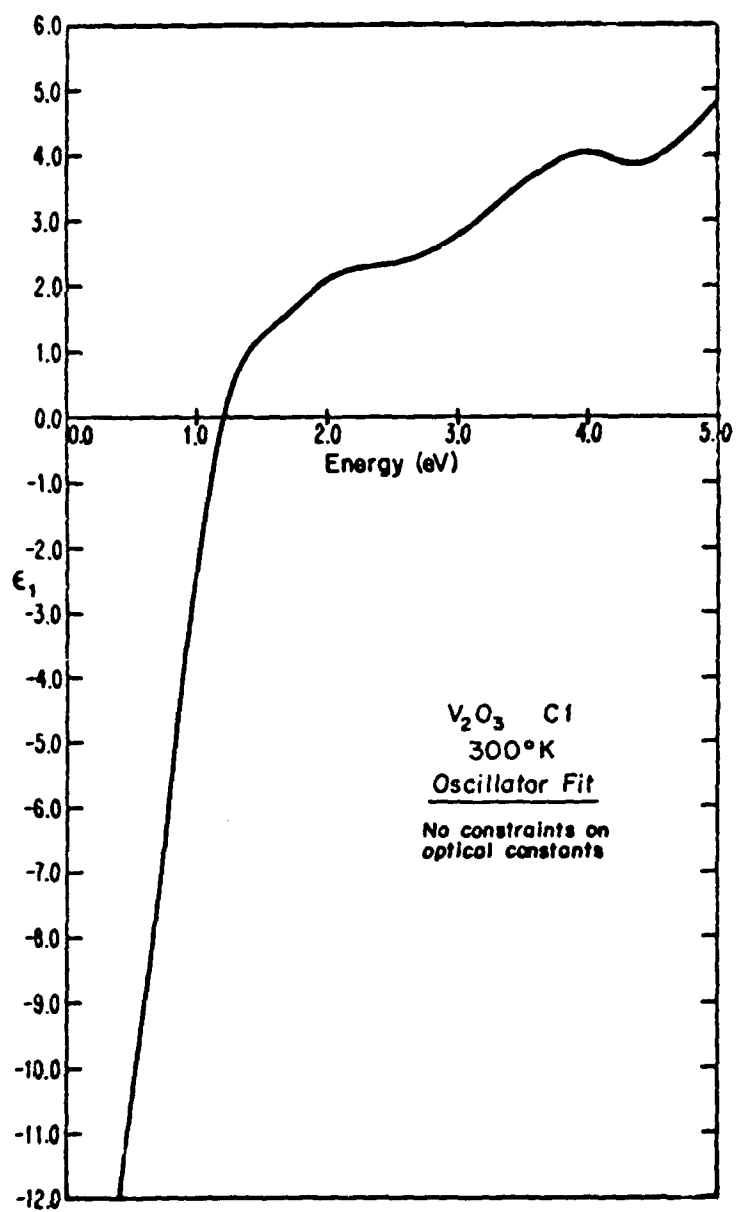
Electrical resistivity vs.  $T^2$  for different samples of  $V_2O_3$ . The reproducibility of the experiment is shown for two separate experiments in the center (open circles and closed squares).

#### j. Dielectric Constant

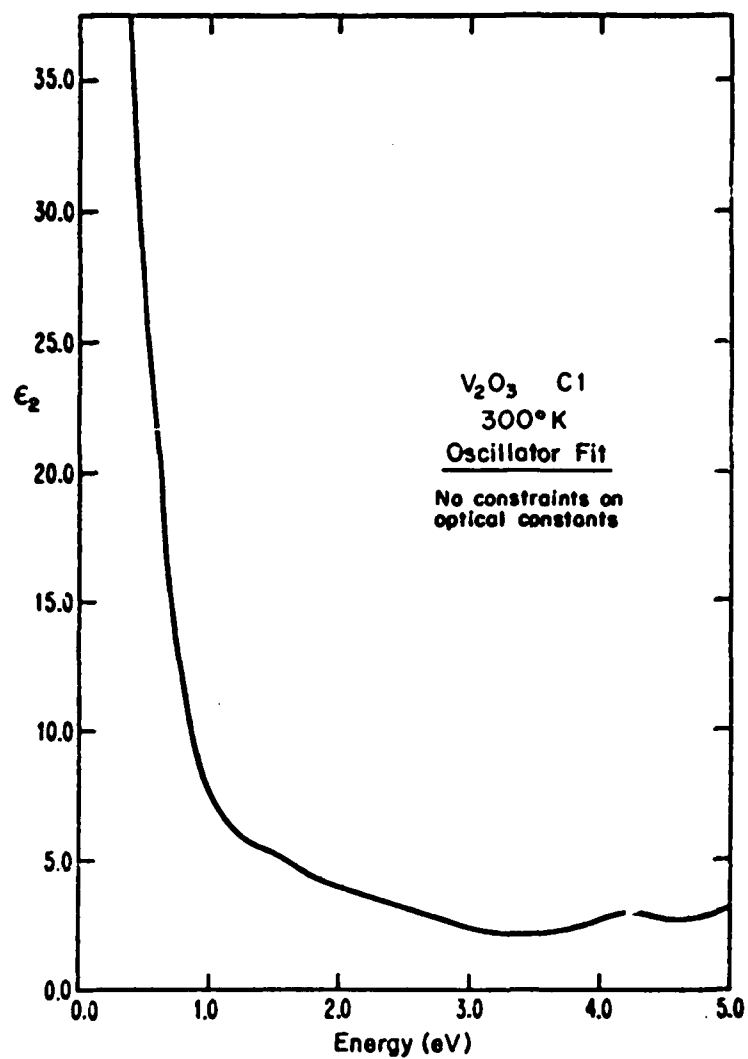
The literature search uncovers the following references:

T062741	E004585
T067613	E053110

Typical data on the dielectric constant of vanadium sesquioxide as taken from E053110 are shown below.



$\epsilon_1$  curve of  $V_2O_3$ .



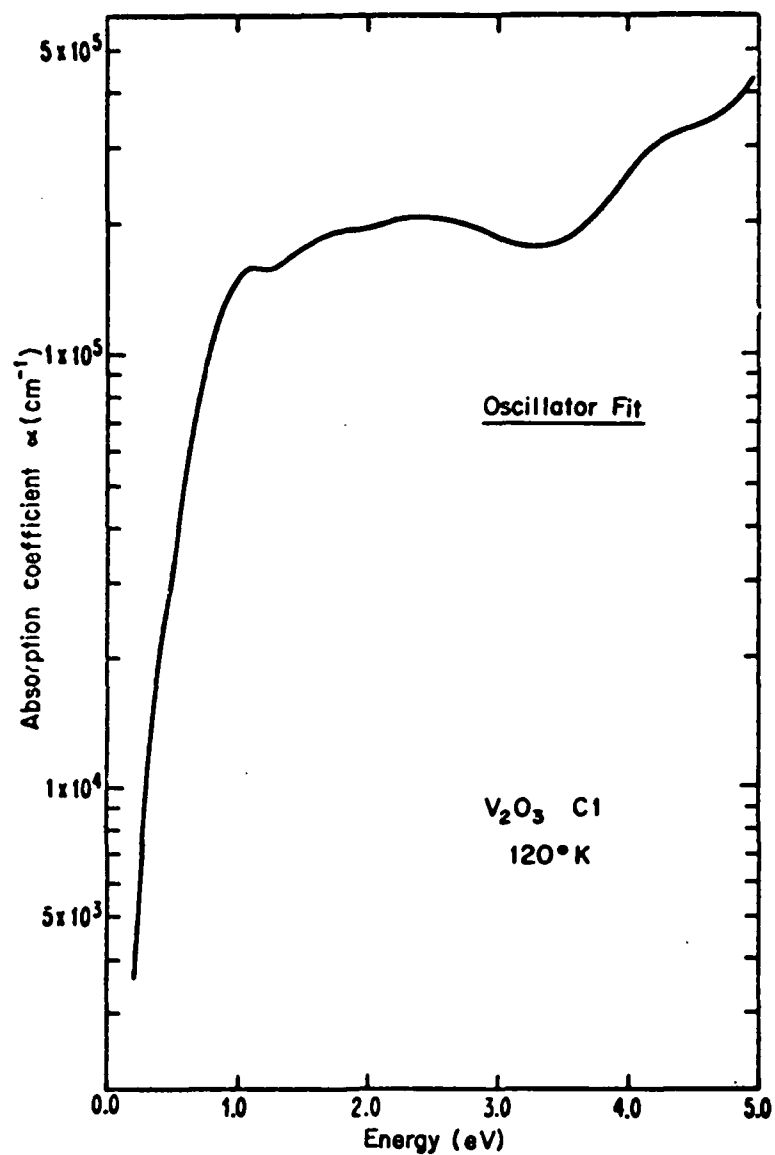
$\epsilon_1$  curve of  $V_2O_3$ .

#### k. Absorption Coefficient

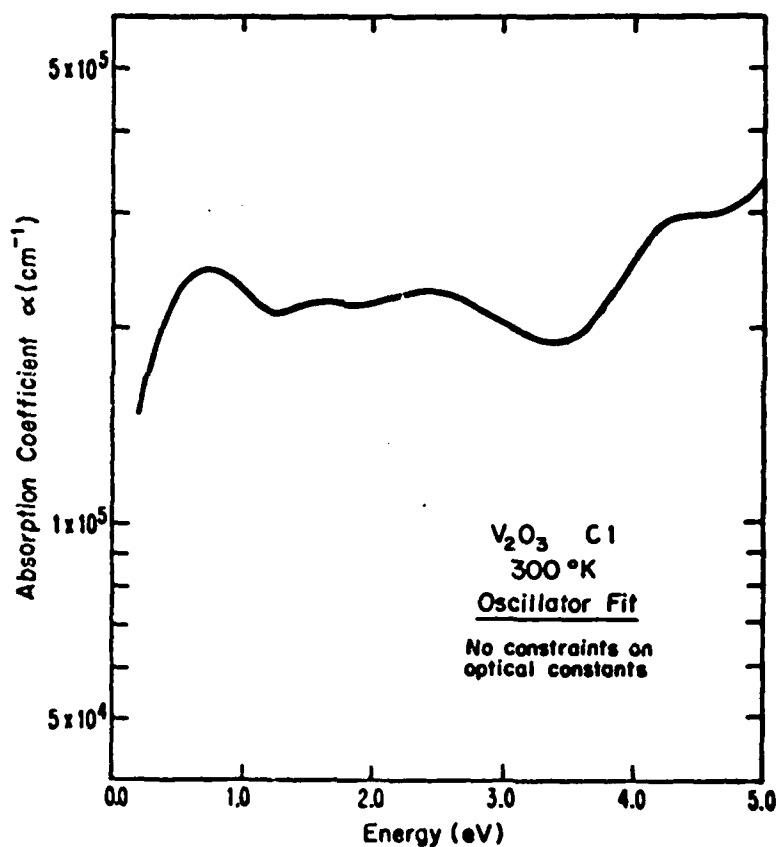
The literature search uncovers the following references:

T062741	T089687
T089293	E053110

Typical data on the absorption coefficient of vanadium sesquioxide as taken from E053110 are shown below.



$\alpha$  curve of  $\text{V}_2\text{O}_3$ .



$\alpha$  curve of  $V_2O_3$ , obtained from another fit.

#### 1. Refractive Index

The literature search uncovers the following references: T062741 and E053110.

Typical data on the refractive index of vanadium sesquioxide as taken from E053110 are shown below.



Optical constants  $n$  and  $k$  of a  $V_2O_3$  crystal (C1) at room temperature, obtained by different methods.

Method	At 1.96 eV		At 2.54 eV	
	$n$	$k$	$n$	$k$
Angular Dependence	1.77	1.10	1.82	0.90
Oscillator Fit using Eq. (3-21b)	1.79	1.10	1.79	0.89
Oscillator Fit using Eq. (3-21a)	1.81	1.10	1.81	0.86
Kramers-Kronig $p = 1.0$	1.83	1.08	1.81	0.86
Kramers-Kronig $p = 1.1$	1.81	1.09	1.79	0.87
Kramers-Kronig $p = 1.2$	1.78	1.09	1.76	0.88
Kramers-Kronig $p = 1.3$	1.76	1.10	1.73	0.8

### 2.3. Vanadium Sesquioxide Doped with Chromium

Like pure vanadium sesquioxide, chromium-doped vanadium sesquioxide  $[(Cr_xV_{1-x})_2O_3]$  exhibits also the low-temperature transition which involves a sudden change in crystal structure (monoclinic to rhombohedral), in electrical properties (semiconducting to metallic), and in magnetic ordering (antiferromagnetic to paramagnetic). Thermal studies [T088468] showed that, with increasing dopant concentration, the transition temperature at first increases from 173 K ( $x=0$ ) to 187 K ( $x=0.033$ ) and then decreases steadily to 151 K ( $x=0.12$ ).

When the dopant concentration is in the range  $0.005 \leq x \leq 0.018$ , the chromium-doped vanadium sesquioxide exhibits another transition in the temperature range 250 to 400 K, depending upon the dopant concentration. This transition at higher temperatures is associated with the  $\alpha$ - $\beta$  phase transformation of the crystal structure. For example [T087463], the  $\alpha$ -corundum form (rhombohedral) of the crystal structure of  $(Cr_{0.01}V_{0.99})_2O_3$ , which is transformed from the  $\gamma$ -phase (monoclinic) at the low-temperature transition around 175 K, exists as a sole phase only in the temperature range from 175 to 275 K and will transform into the  $\beta$ -corundum form completely at about 375 K. Between approximately 275 and 375 K the  $\alpha$ - and  $\beta$ -corundum forms coexist. The thermal

and electrical anomalies occurring at the high-temperature transition region are relatively very small and cover a range of temperature in contrast to the very large anomalies sharply at the transition temperature of the low-temperature transition.

A systematic and exhaustive search of the world literature for the pertinent references on the thermophysical, electrical, and optical properties of chromium-doped vanadium sesquioxide has been conducted and the results are given in the following subsections. Typical data on each of the properties are also presented, if available.

#### a. Thermal Conductivity

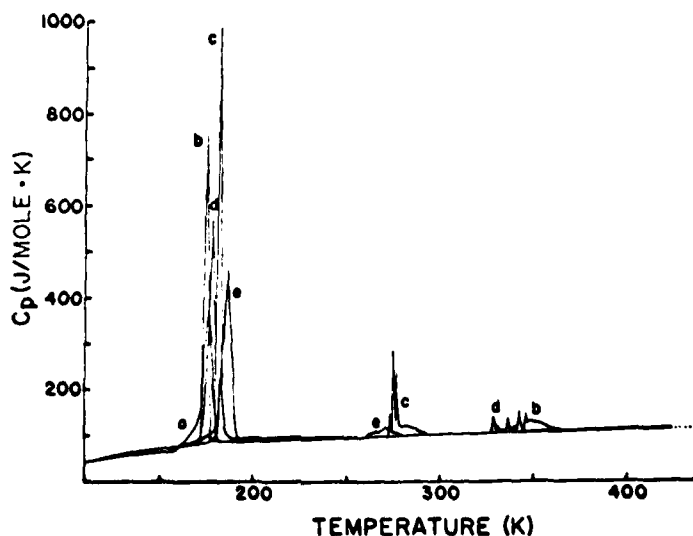
The literature search uncovers no reference on the thermal conductivity.

#### b. Specific Heat

The literature search uncovers the following references:

T073993	T083049	T088468
T081116	T087463	T088798

Typical data on the specific heat of Cr-doped vanadium sesquioxide as taken from T087463 are shown below.



Temperature variation of heat capacity ( $C_p$ ) of pure and doped  $V_2O_5$  with increasing temperature (T): (a)  $V_2O_5$ ; (b)  $(Al_{0.01}V_{0.99})_2O_5$  #2; (c)  $(Al_{0.01}V_{0.99})_2O_5$ ; (d)  $(Cr_{0.01}V_{0.99})_2O_5$ ; (e)  $(Cr_{0.01}V_{0.99})_2O_5$ .

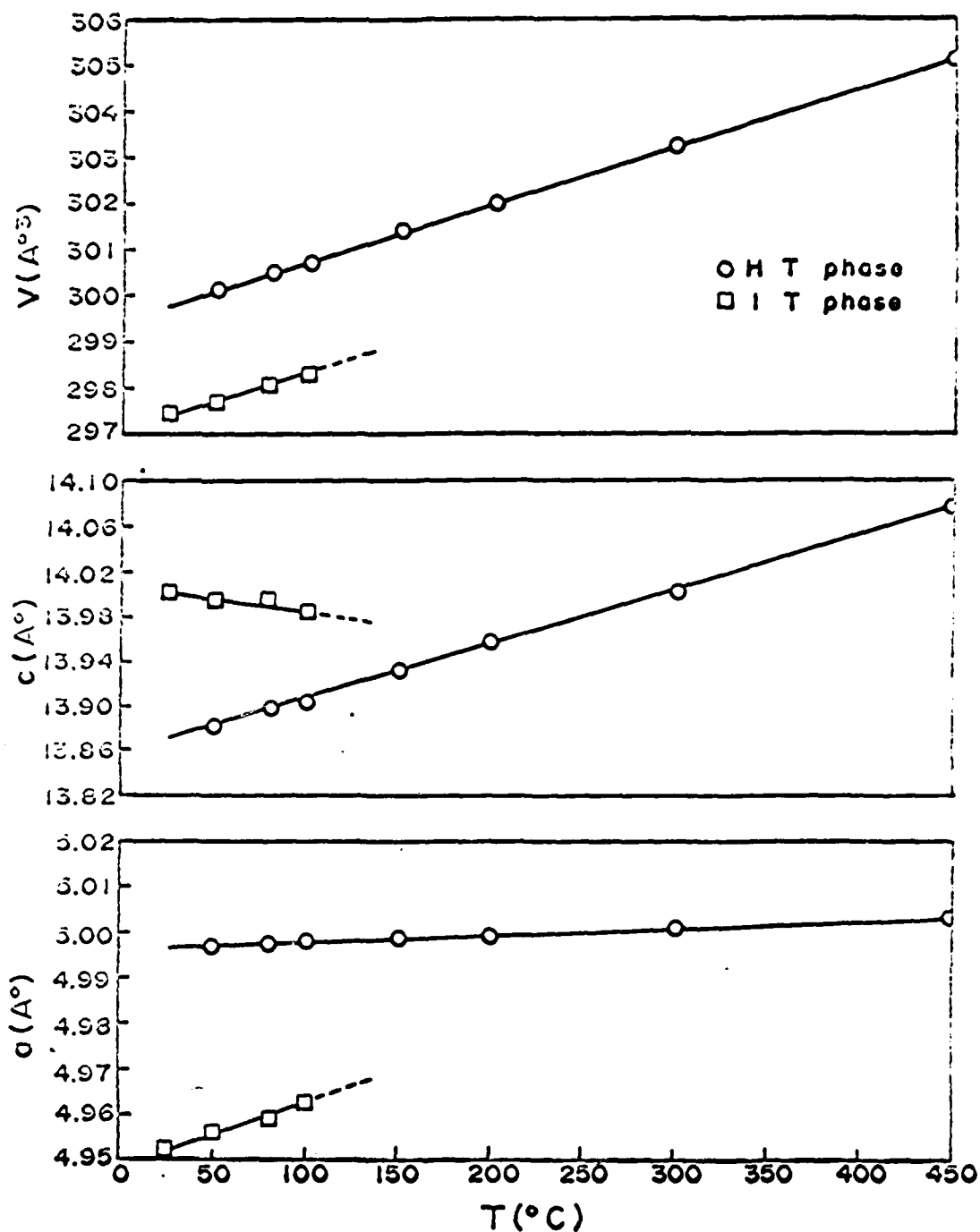
## c. Thermal Linear Expansion

The literature search uncovers the following references: T069622 and T079928.

Typical data on the thermal linear expansion of Cr-doped vanadium sesquioxide as taken from T079928 are shown below.

Lattice parameters for Cr-doped  $V_2O_3$ .

Parameters (at 40°C)	One percent Cr doped $V_2O_3$				$3\%Cr-V_2O_3$
	I.T. Form		H.T. Form		Unannealed
	Annealed	Unannealed	Annealed	Unannealed	
$a(\text{\AA})(\pm 0.003)$	4.954	4.952	4.997	4.995	4.998
$c(\text{\AA})(\pm 0.01)$	14.00	14.00	13.88	13.92	13.92
$V(\text{\AA}^3)(\pm 0.5)$	297.6	297.3	300.1	300.8	301.1
$c/a(\pm 0.004)$	2.826	2.827	2.778	2.787	2.785
$\frac{1}{a} \frac{da}{dT} (\frac{1}{^\circ K})(\pm 0.3 \times 10^{-5})$	$2.7 \times 10^{-5}$	---	$0.3 \times 10^{-5}$	$0.8 \times 10^{-5}$	$1.0 \times 10^{-5}$
$\frac{1}{c} \frac{dc}{dT} (\frac{1}{^\circ K})(\pm 0.3 \times 10^{-5})$	$-1.6 \times 10^{-5}$	---	$3.5 \times 10^{-5}$	$0.4 \times 10^{-5}$	$0.4 \times 10^{-5}$
$\frac{1}{V} \frac{dV}{dT} (\frac{1}{^\circ K})(\pm 1 \times 10^{-5})$	$3.8 \times 10^{-5}$	---	$4.1 \times 10^{-5}$	$2.0 \times 10^{-5}$	$2.4 \times 10^{-5}$



Lattice parameters for annealed  $(\text{Cr}_{0.01}\text{V}_{0.99})_2\text{O}_3$

#### d. Thermal Diffusivity

The literature search uncovers no reference on the thermal diffusivity.

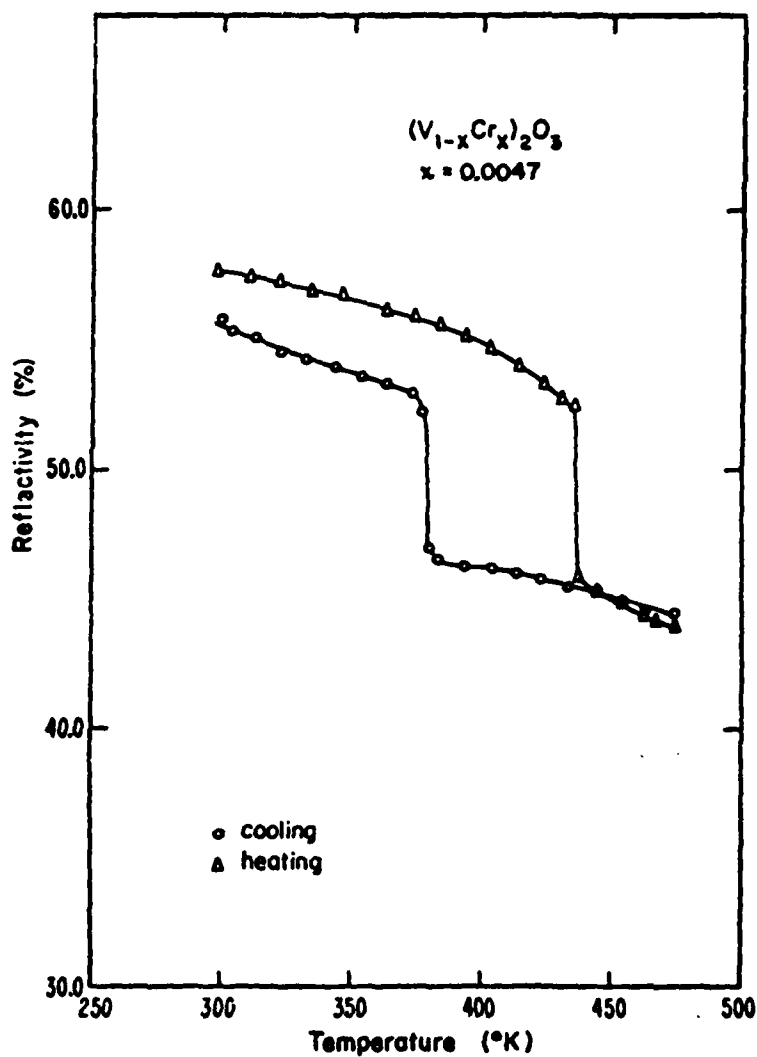
### e. Thermal Emittance

The literature search uncovers no reference on the thermal emittance.

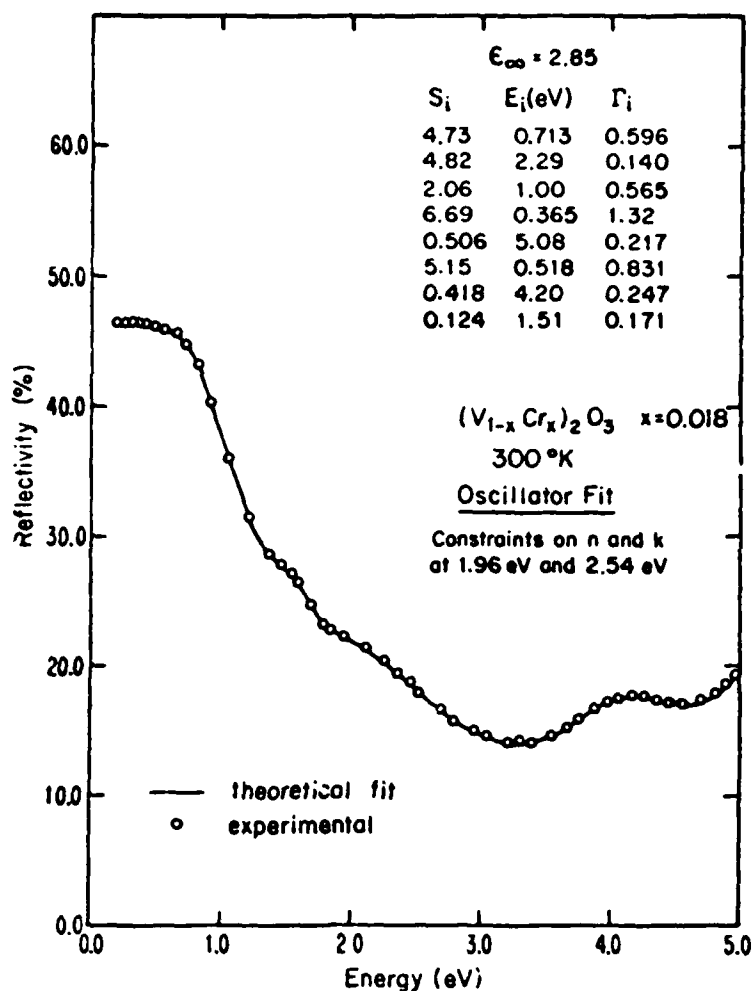
### f. Thermal Reflectance

The literature search uncovers the following reference: E053110.

Typical data on the reflectance of Cr-doped vanadium sesquioxide as taken from E053110 are shown below.



The reflectivity of a  $(V_{1-x}Cr_x)_2O_3$  crystal (where  $x=0.0047$ ) at 0.65 eV as a function of temperature.



A theoretical fit to the experimental reflectivity data of a  $(V_{0.982}Cr_{0.018})_2O_3$  crystal, where the values of  $n$  and  $k$  at 1.96 eV and 2.54 eV are constrained to approach those obtained from the angular dependence measurements.

#### g. Thermal Absorptance

The literature search uncovers no reference on the thermal absorptance.

#### h. Thermal Transmittance

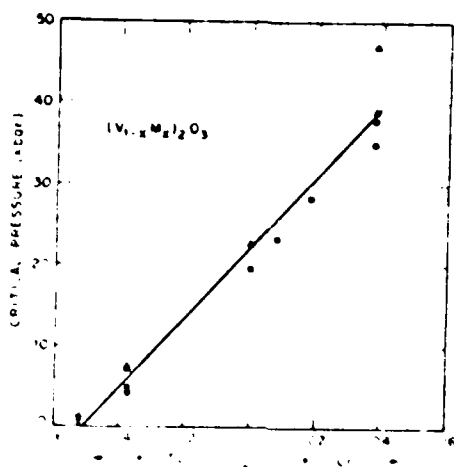
The literature search uncovers no reference on the thermal transmittance.

#### i. Electrical Resistivity

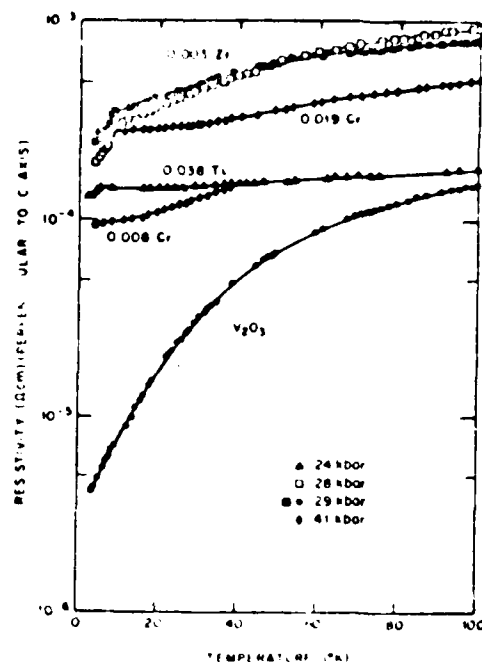
The literature search uncovers the following references:

T069622	E012765	E045575	E073401	E107392	A000153
T073993	E015182	E047288	E088400	A000151	A000154
T079099	E045181	E047489	E104938	A000152	

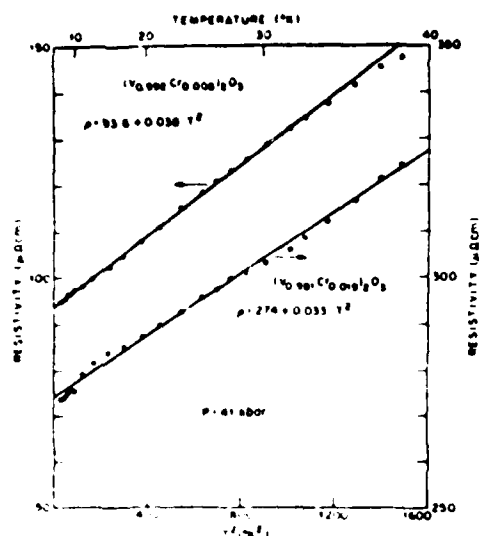
Typical data on the electrical resistivity of Cr-doped vanadium sesquioxide as taken from T069622 are shown below.



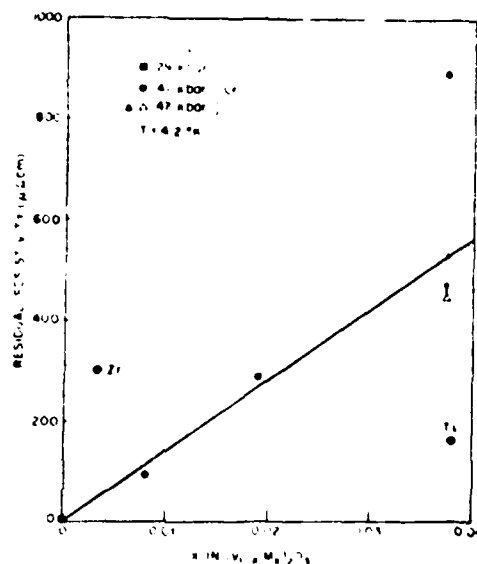
Critical pressure at 4.2 K for the M-AF transition plotted vs. the concentration of Ti or Cr in  $V_2O_3$ . Triangles and circles are for increasing and decreasing pressure, respectively.



Electrical resistivity perpendicular to the c axis vs. temperature for samples of doped  $V_2O_3$  obtained in the metallic phase above the critical pressure for suppression of the AF phase. Note the large increase in the residual resistivity with doping. The reproducibility of the experiment is shown by the two curves for Zr samples from different experiments (open and closed squares).



Electrical resistivity vs.  $T^2$  for two Cr-doped samples. Curves show that  $T^2$  term is unchanged but the residual resistivity increases rapidly on doping  $x=0.008$  Cr, left scale and  $x=0.019$  Cr, right scale. Both samples were run together at 41 kbar.



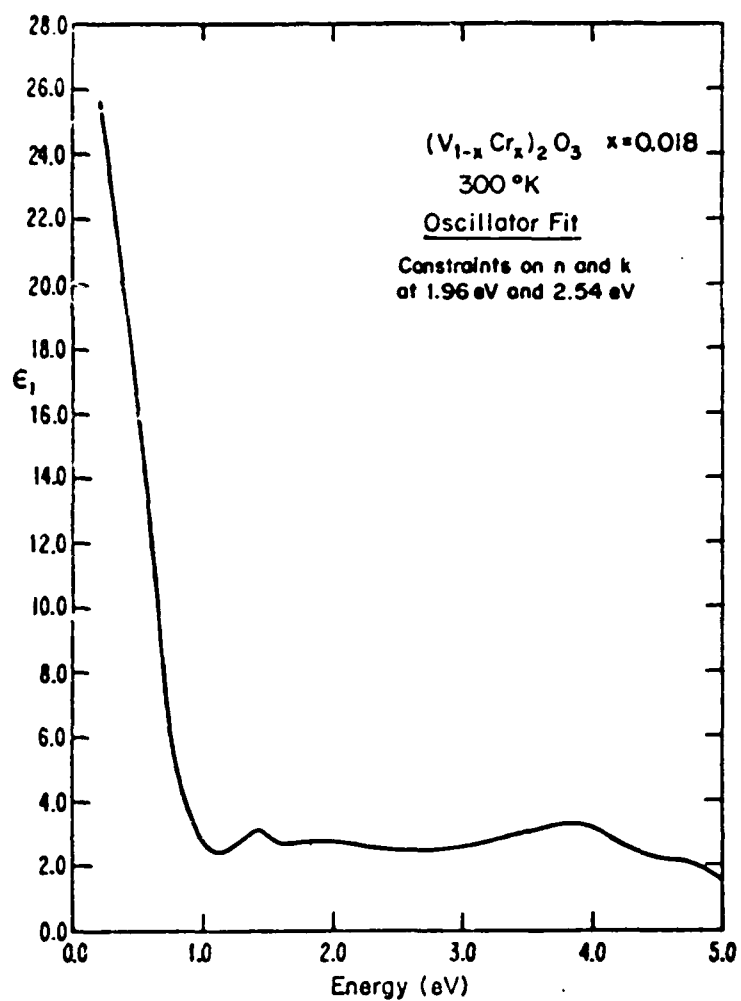
Residual resistivity vs. Cr concentration. The slope is 140  $\mu\Omega/\text{cm}/\text{at.}\%$  Cr. The point at  $x=0.038$  is discussed in the text. For comparison, points for Zr and Ti are included from Fig. 12.

#### j. Dielectric Constant

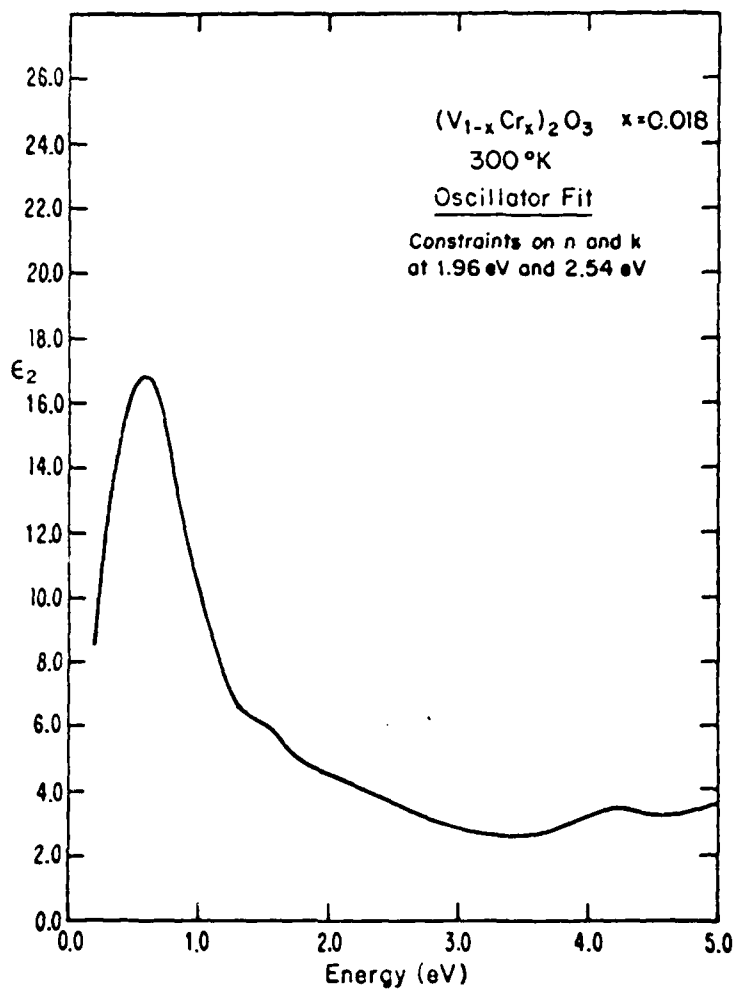
The literature search uncovers the following reference: E053110.

Typical data on the dielectric constant of Cr-doped vanadium sesquioxide as taken from E053110 are shown below.





$\epsilon_1$  curve of the  $(V_{0.982}Cr_{0.018})_2O_3$  crystal.

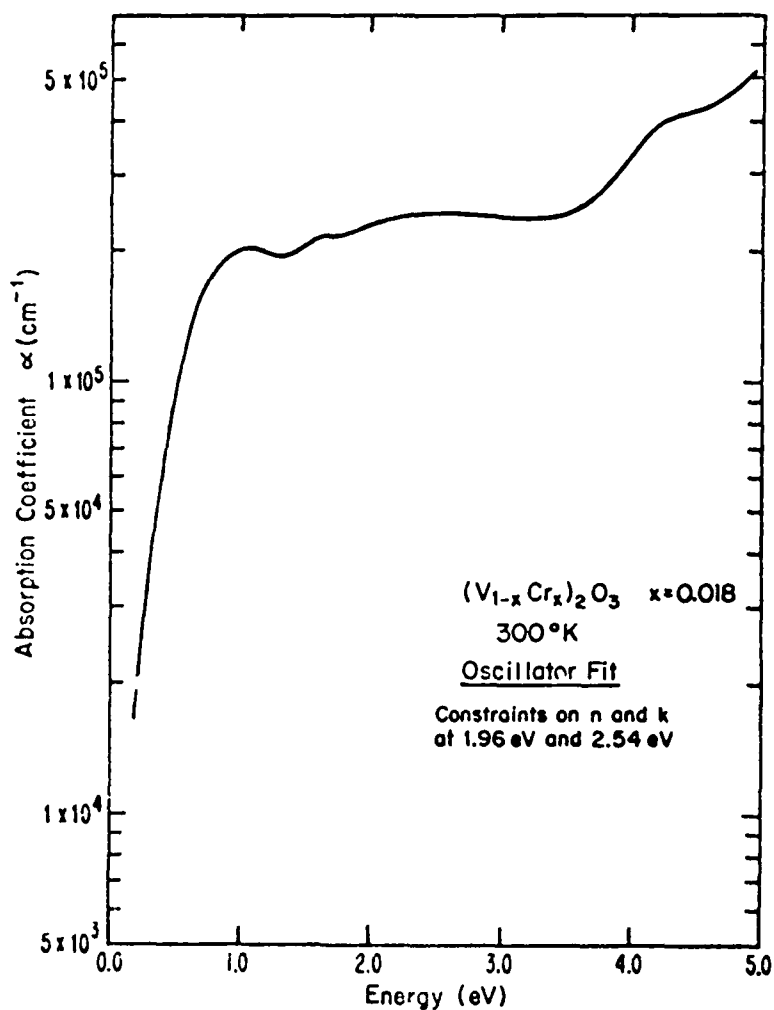


$\epsilon_2$  curve of the  $(V_{0.982}Cr_{0.018})_2O_3$  crystal.

#### k. Absorption Coefficient

The literature search uncovers the following reference: E053110.

Typical data on the absorption coefficient of Cr-doped vanadium sesquioxide as taken from E053110 are shown below.



$\alpha$  curve of the  $(V_{0.982}Cr_{0.018})_2O_3$  crystal.

#### 1. Refractive Index

The literature search uncovers the following reference: E053110.

Typical data on the refractive index of Cr-doped vanadium sesquioxide as taken from E053110 are shown below.

Optical constant  $n$  and  $k$  of a  $(V_{0.982}Cr_{0.018})_2O_3$  crystal (R1) at room temperature, obtained by different methods.

Method	At 1.96 eV		At 2.54 eV	
	$n$	$k$	$n$	$k$
Angular Dependence	2.02	1.14	1.86	0.96
Oscillator Fit using Eq. (3-21b)	2.02	1.14	1.85	0.95
Oscillator Fit using Eq. (3-21a)	2.01	1.13	1.86	0.93
Kramers-Kronig $p = 1.2$	2.05	1.11	1.86	0.92
Kramers-Kronig $p = 1.3$	2.02	1.12	1.83	0.94
Kramers-Kronig $p = 1.4$	1.99	1.14	1.80	0.95
Kramers-Kronig $p = 1.5$	1.95	1.15	1.77	0.96

#### 2.4. Vanadium Sesquioxide Doped with Titanium

Titanium-doped vanadium sesquioxide  $[(Ti_xV_{1-x})_2O_3]$  exhibits also the low-temperature transition which involves a sudden change in crystal structure (monoclinic to rhombohedral), in electrical properties (semiconducting to metallic), and in magnetic ordering (antiferromagnetic to paramagnetic). The addition of titanium ions ( $Ti^{3+}$ ) to vanadium sesquioxide leads, however, to the suppression of the antiferromagnetic semiconducting phase; the metal-to-antiferromagnetic semiconductor transition temperature decreases rapidly as the titanium concentration increases. Raising pressure will also lower the transition temperature. The transition temperature drops to zero and the antiferromagnetic semiconducting phase vanishes as titanium concentration exceeds 5.1 at.%.

Unlike chromium-doped vanadium sesquioxide, there is no high-temperature transition in titanium-doped vanadium sesquioxide.

A systematic and exhaustive search of the world literature for the pertinent references on the thermophysical, electrical, and optical properties of titanium-doped vanadium sesquioxide has been conducted and the results are given in the following subsections. Typical data on each of the properties are also presented, if available.

### a. Thermal Conductivity

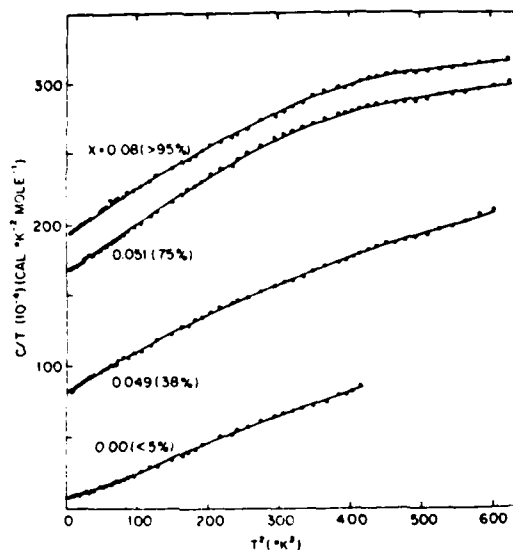
The literature search uncovers no reference on the thermal conductivity.

### b. Specific Heat

The literature search uncovers the following references:

T063535      T070694      T088798

Typical data on the specific heat of Ti-doped vanadium sesquioxide as taken from T063535 are shown below.



The heat capacity of Ti-doped  $\text{V}_2\text{O}_3$  at low temperatures plotted as  $C/T$  vs.  $T^2$  to show the extremely large linear term found in the metallic phase. The numbers in parentheses give the fraction of the sample in the metallic phase as determined by powder x-ray diffraction measurements at 5 K.

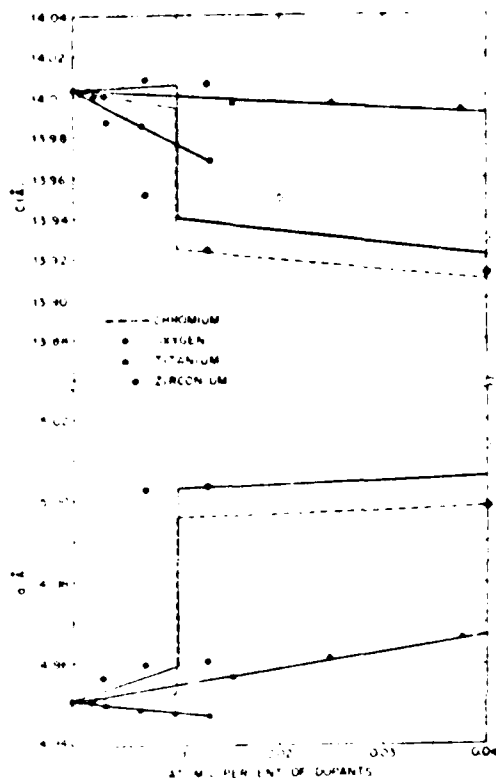
### c. Thermal Linear Expansion

The literature search uncovers the following reference: T069622.

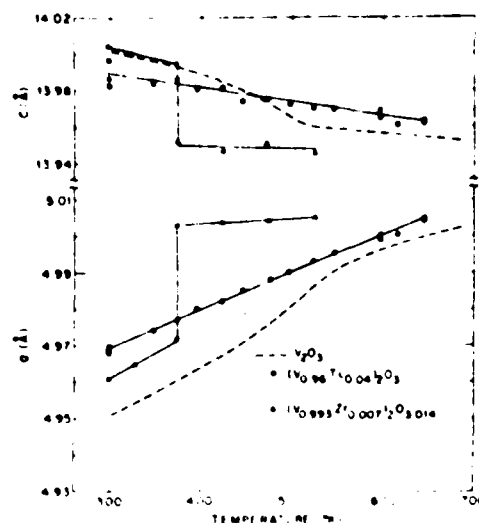
Typical data on the thermal linear expansion of Ti-doped vanadium sesquioxide as taken from T069622 are shown below.

### Coefficients of thermal expansion at 298 K.

Sample No.	$\frac{1}{a} \left( \frac{da}{dT} \right) \times 10^4 \text{ } ^\circ\text{K}^{-1}$	$\frac{1}{c} \left( \frac{dc}{dT} \right) \times 10^4 \text{ } ^\circ\text{K}^{-1}$
<b>Metallic phase</b>		
$x = 0.00$	$20.2 \pm 0.3$	$-8.6 \pm 0.3$
0.04 Ti	20.4	-5.6
4-mole% MgO	$25.5 \pm 2.0$	$-9.5 \pm 2.0$
16-mole% $\text{Fe}_2\text{O}_3$	$15.0 \pm 1.0$	$-4.4 \pm 2.0$
<b>Insulating phase</b>		
0.038 Cr	$8.8 \pm 1.0$	$3.5 \pm 1.0$
4-mole% $\text{ZrO}_2$	$8.8 \pm 1.0$	$3.5 \pm 1.0$
4-mole% $\text{ZrO}_2$	$11.3 \pm 2.0$	$\approx 0 \pm 2$



Lattice parameters of  $(\text{V}_{1-x}\text{M}_x)_2\text{O}_3$  vs.  $x$  for different dopants M at room temperature. The closed symbols are this work; open symbols, Ref. 8. The dashed curve is for  $\text{M}=\text{Cr}$  after Ref. 2.



Lattice parameters vs. temperature for samples of doped  $\text{V}_2\text{O}_3$  showing the M-I transition in a Zr-doped sample and the absence of a high-temperature anomaly in a Ti-doped sample. The dashed curves are for pure  $\text{V}_2\text{O}_3$  after Ref. 2.

#### d. Thermal Diffusivity

The literature search uncovers no reference on the thermal diffusivity.

#### e. Thermal Emittance

The literature search uncovers no reference on the thermal emittance.

f. Thermal Reflectance

The literature search uncovers no reference on the thermal reflectance.

g. Thermal Absorptance

The literature search uncovers no reference on the thermal absorptance.

h. Thermal Transmittance

The literature search uncovers no reference on the thermal transmittance.

i. Electrical Resistivity

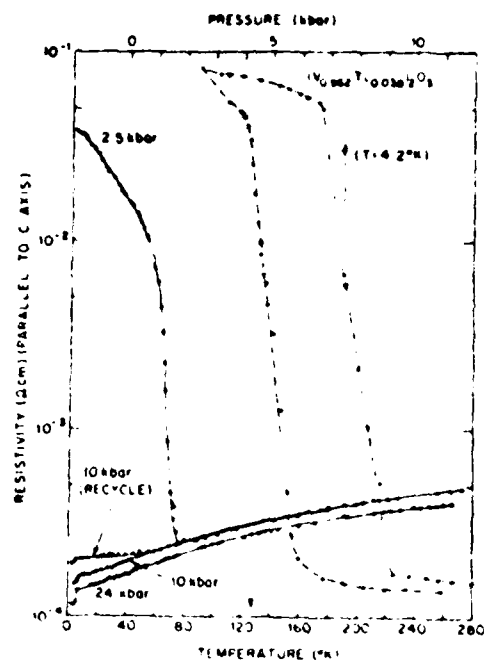
The literature search uncovers the following references:

T069622	T088278	E015182	E103431	A000154	A000156
T070694	E012765	E091263	E105237	A000155	

Typical data on the electrical resistivity of Ti-doped vanadium sesquioxide as taken from T069622 are shown below.

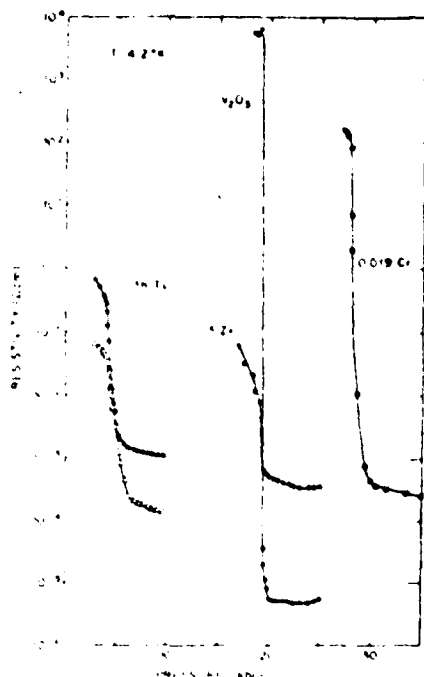


Comparison of the electrical resistivity perpendicular to the c axis vs. temperature for doped samples of  $V_2O_3$ . The dashed lines for  $V_2O_3$  and the Cr-doped sample are from Ref. 2. Note presence or absence of high-temperature transition and the low resistivity in the AF phase of the Zr-doped sample.

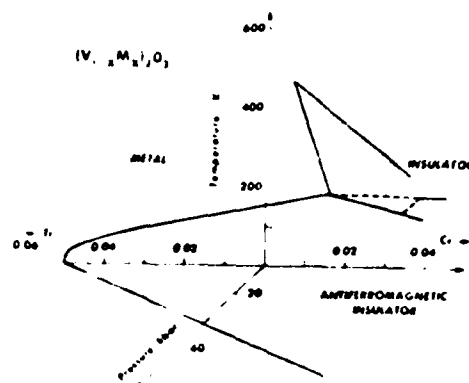


Electrical resistivity parallel to the c axis vs. temperature for  $(V_{0.962}Ti_{0.038})_2O_3$  at several pressures showing the suppression of AF phase. Note deterioration of sample after cycling through the M-AF transition. Dashed curves are the resistivity of 4.2 K vs. pressure (upper scale) showing the hysteresis in the M-AF transition.





Electrical resistivity perpendicular to the c axis (closed symbols) vs. pressure at 4.2 K for doped  $V_2O_3$ . All curves are for decreasing pressure. The two Ti curves are from two crystals mounted in the high-pressure apparatus together but with different orientation thus showing deviations from true hydrostatic conditions in the experiment.



Temperature-pressure-composition phase diagram showing M-I, M-AF, and I-AF surfaces. M-I surface terminates at a solid-solid critical line.

#### j. Dielectric Constant

The literature search uncovers no reference on the dielectric constant.

#### k. Absorption Coefficient

The literature search uncovers no reference on the absorption coefficient.

#### l. Refractive Index

The literature search uncovers no reference on the refractive index.

## 2.5. Trivanadium Pentoxide

Trivanadium pentoxide ( $V_3O_5$ ) is a paramagnetic semiconductor with a monoclinic crystal structure. It is reported to have a very narrow range of homogeneity. Unlike  $V_2O_3$  or  $VO_2$ , trivanadium pentoxide does not exhibit a metal-semiconductor transition at any temperature. In fact, metal-semiconductor transitions have been found in all members of the homologous series between  $V_2O_3$  and  $VO_2$  of general formula  $V_nO_{2n-1}$  (where  $n=3$  to 9) except  $V_3O_5$  and  $V_7O_{13}$ ; the latter is reported to be a metal. Trivanadium pentoxide melts at about 2100 K. Its density is  $4.55 \text{ g cm}^{-3}$  at room temperature.

A crystallographic phase transition occurs in trivanadium pentoxide at about 425 K. This transition involves only a small change in the monoclinic lattice parameters and in the cell volume without change of the crystal symmetry. However, anomalies in thermal, electrical, and magnetic properties have all been observed at this transition. Above the transition temperature the crystal remains to be a semiconductor.

A systematic and exhaustive search of the world literature for the pertinent references on the thermophysical, electrical, and optical properties of trivanadium pentoxide has been conducted and the results are given in the following subsections. Typical data on each of the properties are also presented, if available.

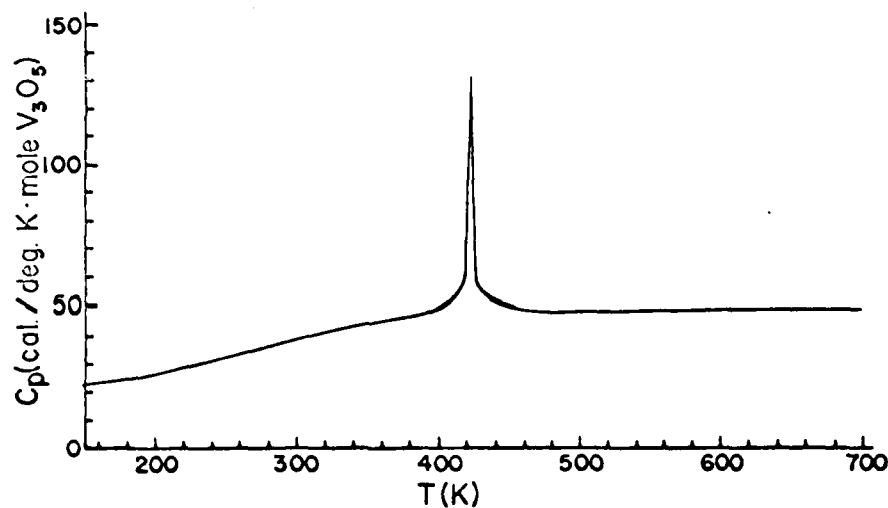
### a. Thermal Conductivity

The literature search uncovers no reference on the thermal conductivity.

### b. Specific Heat

The literature search uncovers the following references: T088469 and A000157.

Typical data on the specific heat of trivanadium pentoxide as taken from T088469 are shown below.

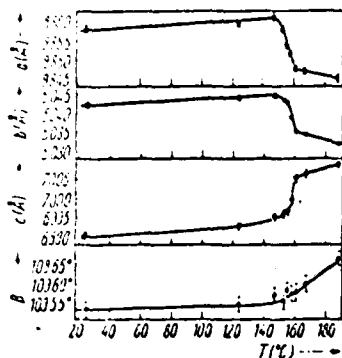


Temperature variation of heat capacity of  $V_3O_5$  (T increasing).

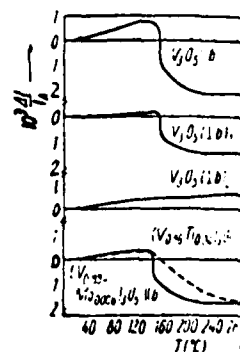
### c. Thermal Linear Expansion

The literature search uncovers the following reference: T084931.

Typical data on the thermal linear expansion of trivanadium pentoxide as taken from T084931 are shown below.



Temperature dependence of the parameters of the monoclinic unit cell.



Expansion behaviour of  $V_3O_5$  [( $lb$ )<sub>1</sub> perpendicular to ( $lb$ )<sub>2</sub>, no preferred crystallographic directions].

### d. Thermal Diffusivity

The literature search uncovers no reference on the thermal diffusivity.

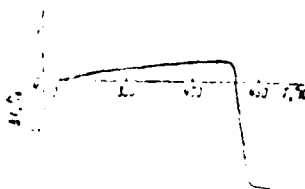
#### e. Thermal Emittance

The literature search uncovers no reference on the thermal emittance.

#### f. Thermal Reflectance

The literature search uncovers the following reference: T076435.

Typical data on the thermal reflectance of trivanadium pentoxide as taken from T076435 are shown below.



Temperature dependence of the coefficient of reflection of visible light from  $V_3O_5$ . Here,  $\Delta R$  is the change in the reflection coefficient relative to its value at room temperature.

#### g. Thermal Absorptance

The literature search uncovers no reference on the thermal absorptance.

#### h. Thermal Transmittance

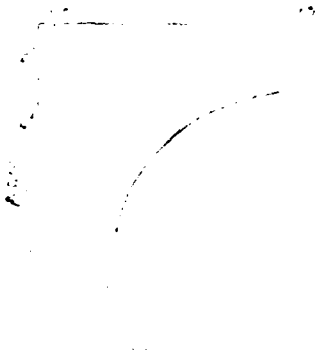
The literature search uncovers no reference on the thermal transmittance.

#### i. Electrical Resistivity

The literature search uncovers the following references:

T076435	E024796	E051150	E087881	E106761	A000133	A000159
T084931	E041170	E061379	E100203	A000131	A000148	
T089295	E048687	E082690	E102814	A000132	A000158	

Typical data on the electrical resistivity of trivanadium pentoxide as taken from T076435 are shown below.



Temperature dependence of the resistivity of  $V_3O_5$ .

#### j. Dielectric Constant

The literature search uncovers no reference on the dielectric constant.

#### k. Absorption Coefficient

The literature search uncovers no reference on the absorption coefficient.

#### l. Refractive Index

The literature search uncovers the following reference: E102368. However, typical data on the refractive index of trivanadium pentoxide cannot be given since this document only describes an experimental method for measuring the refractive index of trivanadium pentoxide and does not report any data.

### 2.6. Titanium Sesquioxide

Titanium sesquioxide ( $Ti_2O_3$ ) is a dark purple-violet paramagnetic p-type semiconductor at room temperature with a rhombohedral (hexagonal) crystal structure. It exists with a rather narrow range of homogeneity from  $TiO_{1.49}$  to  $TiO_{1.51}$ . It melts at about 2400 K and boils at about 3300 K. Its density is about  $4.6 \text{ g cm}^{-3}$  at room temperature.

A semiconductor-metal transition occurs in titanium sesquioxide around 450 K, at which the rhombohedral lattice parameters also change but the crystal symmetry remains the same. Anomalies in thermal, electrical, magnetic, and other properties have been observed at the transition region. This transition stretches over a temperature range of about 250 degrees, and is due to the crossing of two electron energy bands as an accompaniment of a shift in atomic positions in the crystal.

A systematic and exhaustive search of the world literature for the pertinent references on the thermophysical, electrical, and optical properties of titanium sesquioxide has been conducted and the results are given in the following subsections. Typical data on each of the properties are also presented, if available.

#### a. Thermal Conductivity

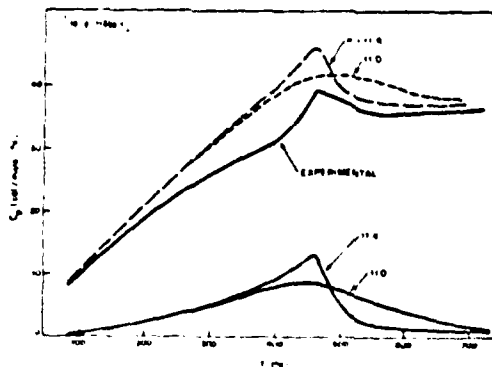
The literature search uncovers the following reference: T066154. This document reports a value of  $0.044 \pm 0.004 \text{ W cm}^{-1}\text{K}^{-1}$  for the thermal conductivity of titanium sesquioxide at 300 K.

#### b. Specific Heat

The literature search uncovers the following references:

T005622	T018971	T069659	T070696	T077803	E060578
T007001	T061741	T070202	T070698	T085437	E086761
T007006	T064004	T070653	T071391	T088479	A000066
T007830	T065865	T070694	T071973	T088935	

Typical data on the specific heat of titanium sesquioxide as taken from T077803 are shown below.



( $C_p$ ) calculated compared with experiment for pure  $\text{Ti}_2\text{O}_3$  model.

#### c. Thermal Linear Expansion

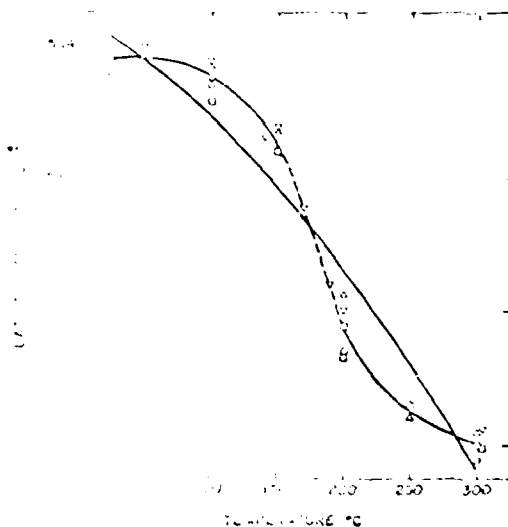
The literature search uncovers the following references:

T046947	T049323	T063516	T066154	T071059
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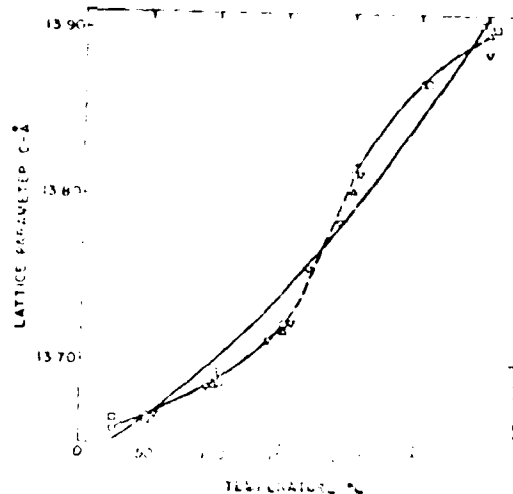
Typical data on the thermal linear expansion of titanium sesquioxide as taken from T071059 are shown below.

Lattice parameters and expansion coefficients of  $Ti_2O_3$ .

	$T = 100^\circ C$	$T = 100^\circ C$
$a = 5.1131 - 4.636 \times 10^{-5} T + 7.639 \times 10^{-7} T^2 \text{ \AA}$	$a = 5.1131 - 4.636 \times 10^{-5} T + 7.639 \times 10^{-7} T^2 \text{ \AA}$	$a = 5.1424 - 6.027 \times 10^{-5} T - 1.601 \times 10^{-7} T^2 \text{ \AA}$
$\alpha_a = -9.116 \times 10^{-6} + 2.947 \times 10^{-7} T + 7.619 \times 10^{-9} T^2 / ^\circ C$	$\alpha_a = -9.116 \times 10^{-6} + 2.947 \times 10^{-7} T + 7.619 \times 10^{-9} T^2 / ^\circ C$	$\alpha_a = -11.729 \times 10^{-6} - 7.662 \times 10^{-7} T - 2.403 \times 10^{-9} T^2 / ^\circ C$
$c = 13.673 + 5.113 \times 10^{-3} T - 4.510 \times 10^{-4} T^2 \text{ \AA}$	$c = 13.673 + 5.113 \times 10^{-3} T - 4.510 \times 10^{-4} T^2 \text{ \AA}$	$c = 13.689 + 4.734 \times 10^{-3} T + 1.12 \times 10^{-4} T^2 \text{ \AA}$
$\alpha_c = 2.11 \times 10^{-4} - 6.695 \times 10^{-7} T - 6.007 \times 10^{-9} T^2 / ^\circ C$	$\alpha_c = 2.11 \times 10^{-4} - 6.695 \times 10^{-7} T - 6.007 \times 10^{-9} T^2 / ^\circ C$	$\alpha_c = 2.11 \times 10^{-4} - 6.695 \times 10^{-7} T - 6.007 \times 10^{-9} T^2 / ^\circ C$



a axis lattice parameter of corundum structure  $Ti_2O_3$ .



c axis lattice parameter of corundum structure  $Ti_2O_3$ .

## d. Thermal Diffusivity

The literature search uncovers no reference on the thermal diffusivity.

## e. Thermal Emittance

The literature search uncovers no reference on the thermal emittance.

## f. Thermal Reflectance

The literature search uncovers the following references:

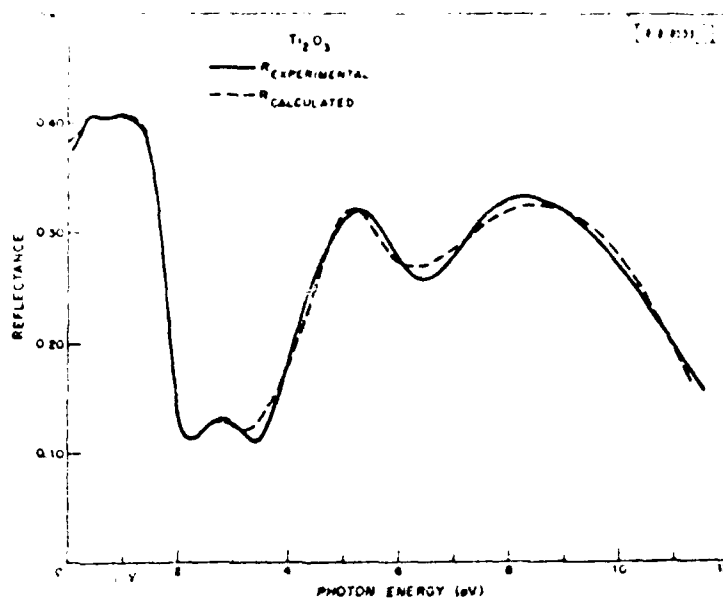
T077689

T079100

E043549

E102158

Typical data on the thermal reflectance of titanium sesquioxide as taken from E043549 are shown below.



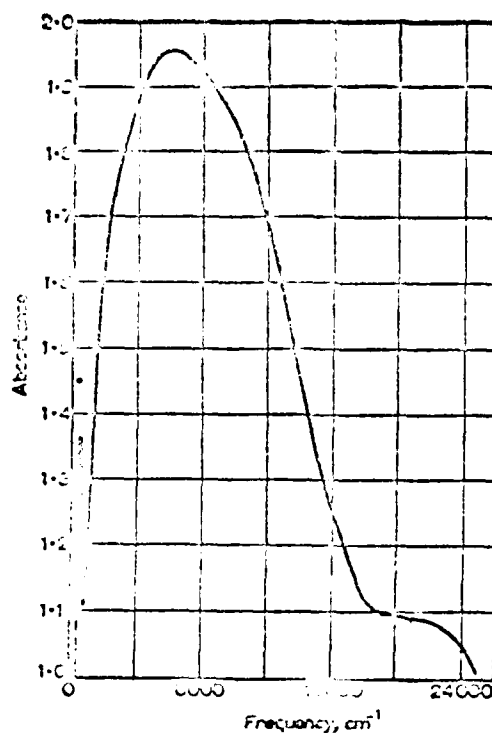
Experimental and calculated reflectance of  $Ti_2O_3$ .

#### g. Thermal Absorptance

The literature search uncovers the following reference: T063516.

Typical data on the thermal absorptance of titanium sesquioxide as taken from T063516 are shown below.



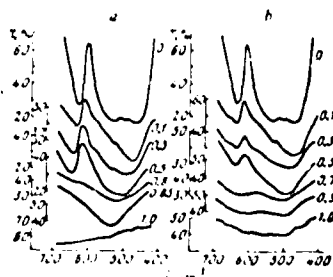


Absorption spectrum of  $\text{Ti}_2\text{O}_3$  ( $1.3 \text{ mg/cm}^2$  in pressed KBr disk).

#### h. Thermal Transmittance

The literature search uncovers the following reference: T068160.

Typical data on the thermal transmittance of titanium sesquioxide as taken from T068160 are shown below.



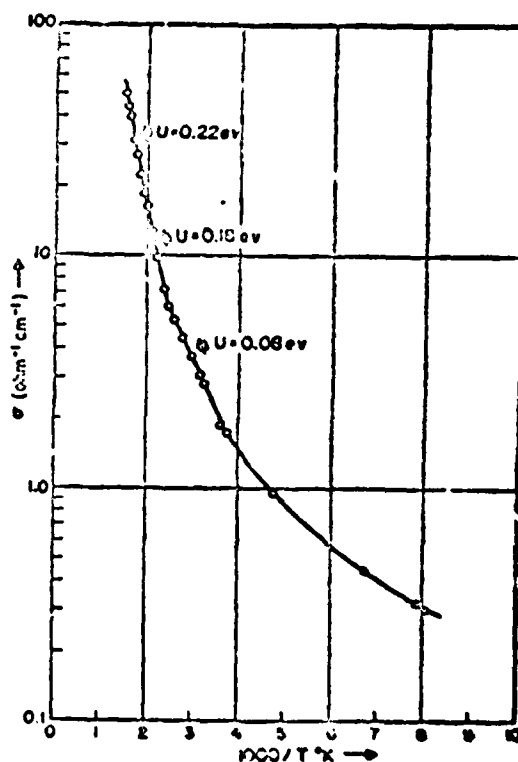
Infrared spectra of solid solutions of scandium oxide with titanium (III) and vanadium (III) oxides: a)  $(\text{Sc}_{1-x}\text{V}_x)_2\text{O}_3$ ; b)  $(\text{Sc}_{1-x}\text{Ti}_x)_2\text{O}_3$ . The numbers against the curves give the value of x for each specimen.

### i. Electrical Resistivity

The literature search uncovers the following references:

T063516	T088479	E011682	E035356	E052020	E068033	E104938	A000072
T070694	E002291	E012944	E036396	E052970	E069075	A000067	A000073
T071391	E002579	E019012	E037145	E054886	E085575	A000068	A000074
T077803	E003081	E027461	E043005	E056498	E086761	A000069	A000075
T079628	E005455	E027472	E044664	E060578	E088400	A000070	
T085437	E010442	E033006	E047086	E062056	E095576	A000071	

Typical data on the electrical resistivity of titanium sesquioxide as taken from T063516 are shown below.



Conductivity/temperature characteristic for  $\text{Ti}_3\text{O}_2$ .

### j. Dielectric Constant

The literature search uncovers the following references:

E04585	E043549	E051442	E102158
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Typical data on the dielectric constant of titanium sesquioxide as taken from E04585 are shown below.

Dielectric constant of  $\text{Me}_2\text{O}_3$  oxides, where Me = Ti, V, Cr, Mn, and Fe. (Subscripts T <  $\theta_{tr}$  and T >  $\theta_{tr}$  indicate that the value of the dielectric constant pertains to a region below or above the transformation temperatures, respectively.)

Oxide .....	$\text{Ti}_2\text{O}_3$	$\text{V}_2\text{O}_5$	$\text{Cr}_2\text{O}_3$	$\text{Mn}_2\text{O}_3$	$\alpha\text{-Fe}_2\text{O}_3$
Dielectric Constant .....	$30_{T < \theta_{tr}}$	$18_{T < \theta_{tr}}$ $(30_{T > \theta_{tr}})$	8	8	12

#### k. Absorption Coefficient

The literature search uncovers no reference on the absorption coefficient.

##### 1. Refractive Index

The literature search uncovers no reference on the refractive index.

#### 2.7. Niobium Dioxide

Niobium dioxide ( $\text{NbO}_2$ ) is a black n-type intrinsic semiconductor with a tetragonal crystal structure. It melts at about 2275 K and boils at about 3800 K. Its density is  $5.98 \text{ g cm}^{-3}$  at room temperature.

A second order phase transition occurs in niobium dioxide around 1070 K, which appears to be caused by a softening of the vibrational modes of the crystalline lattice. This vibrational modes softening exists above the transition temperature, below which the soft-mode distortion disappears. Anomalies in thermal, electrical, magnetic, and other properties have been observed at this transition, at which niobium dioxide transforms from a semiconducting to a metallic state. However, some authors have also reported that it remains to be semiconducting after the transition.

It has been reported that under an applied electric field niobium dioxide switches from a high (greater than 10,000 ohms) to a low (approximately 10 ohms) resistance in a time less than 0.7 nanosecond. The electrical current carrying capability is higher than 80 amperes for pulse durations of several nanoseconds.

A systematic and exhaustive search of the world literature for the pertinent references on the thermophysical, electrical, and optical properties of niobium dioxide has been conducted and the results are given in the following subsections. Typical data on each of the properties are also presented, if available.

a. Thermal Conductivity

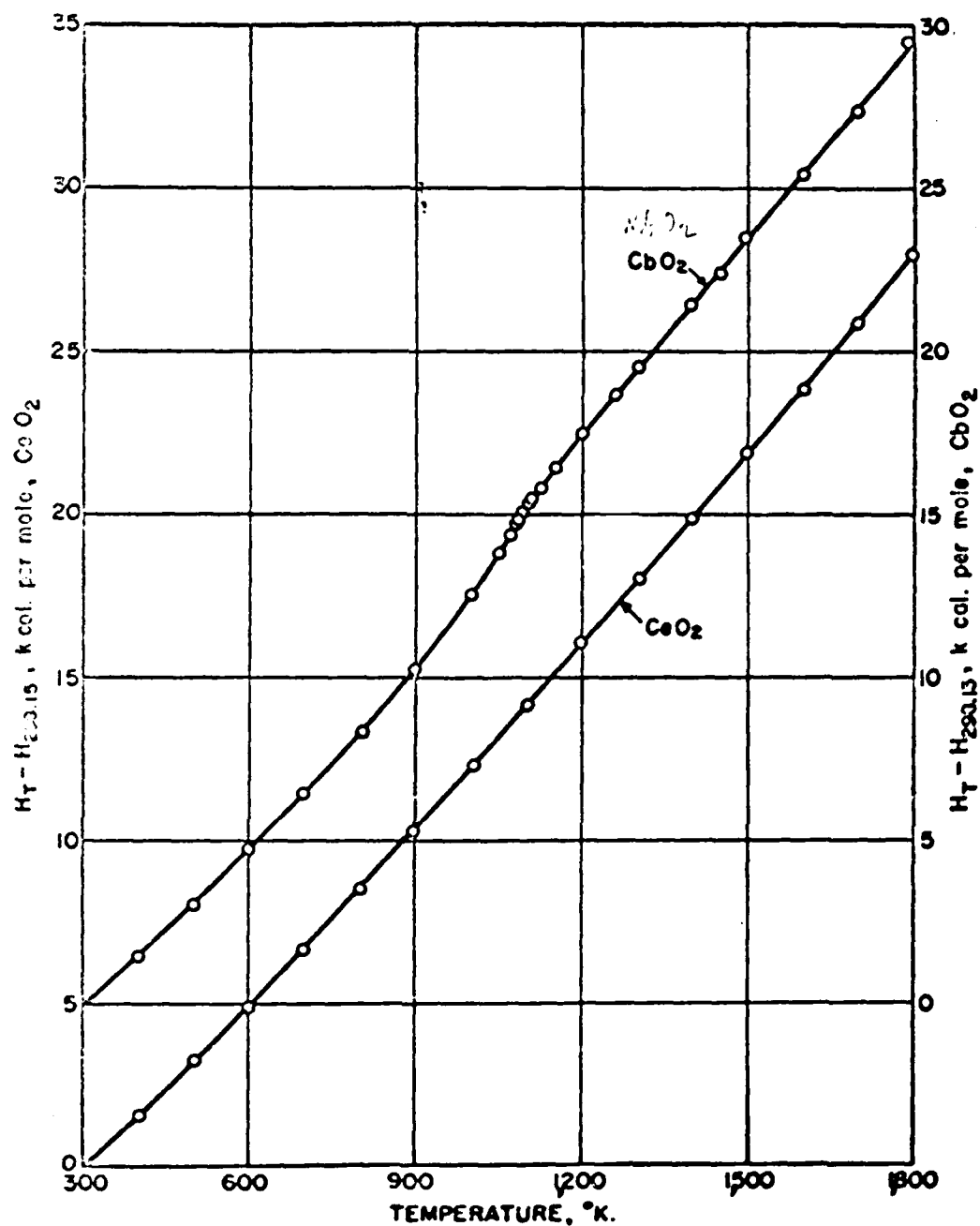
The literature search uncovers no reference on the thermal conductivity.

b. Specific Heat

The literature search uncovers the following references:

T007006	T018112	T025326	T027408	T052954
T015923	T020317	T026427	T029312	T090530

Typical data on the specific heat of niobium dioxide as taken from T029312 are shown below.

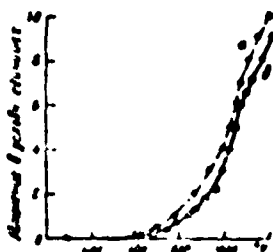


Heat contents of cerium dioxide and columbium dioxide above 298.15 K.

#### c. Thermal Linear Expansion

The literature search uncovers the following reference: T020317.

Typical data on the thermal linear expansion of niobium dioxide as taken from T020317 are shown below.



Thermal expansion curves of two specimens (a,b) of  $\text{NbO}_2$ .

d. Thermal Diffusivity

The literature search uncovers no reference on the thermal diffusivity.

e. Thermal Emittance

The literature search uncovers no reference on the thermal emittance.

f. Thermal Reflectance

The literature search uncovers no reference on the thermal reflectance.

g. Thermal Absorptance

The literature search uncovers no reference on the thermal absorptance.

h. Thermal Transmittance

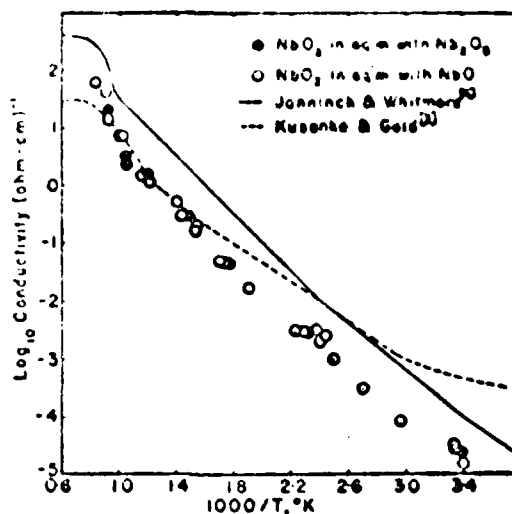
The literature search uncovers no reference on the thermal transmittance.

i. Electrical Resistivity

The literature search uncovers the following references:

E025843	E055117	E084265	A000029
E038875	E071059	E104938	A000030
E039417	E073303	A000027	A000031
E051307	E081115	A000028	A000032

Typical data on the electrical resistivity of niobium dioxide as taken from E039417 are shown below.

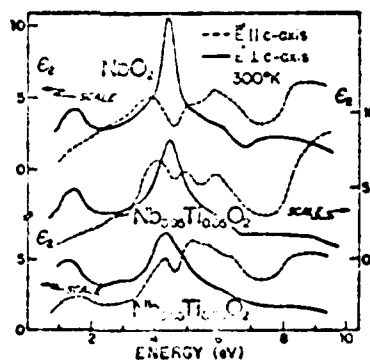


The effects of temperature and oxygen activity on the electrical conductivity of  $\text{NbO}_2$ .

#### j. Dielectric Constant

The literature search uncovers the following reference: E102158.

Typical data on the dielectric constant of niobium dioxide as taken from E102158 are shown below.



Spectral dependence of  $\epsilon_2$  for  $\text{Nb}_{1-x}\text{Ti}_x\text{O}_2$  for  $x = 0$ , 0.05 and 0.20 for light polarized  $\parallel$  and  $\perp$  to the  $c$ -axis.

#### k. Absorption Coefficient

The literature search uncovers no reference on the absorption coefficient.

#### l. Refractive Index

The literature search uncovers no reference on the refractive index.

## 2.8. Europium Monoxide

Europium monoxide ( $\text{EuO}$ ) is a purple ferromagnetic semiconductor or insulator (if pure and stoichiometric) with a face-centered cubic crystal structure of the NaCl type. It becomes paramagnetic above the Curie temperature of 69.29 K. Its density is about  $8.16 \text{ g cm}^{-3}$  at room temperature. Europium monoxide sublimates in vacuum above 970 K and melts at about 2270 K.

Under high pressure (above 300 kbar) pure stoichiometric europium monoxide undergoes an insulator-metal transition; it suddenly changes lattice parameter and becomes metallic at a critical pressure. The mechanism of this transition has been suggested as the promotion of a europium  $4f^7$  electron into the 5d band with an accompanying change in the ion size of  $\text{Eu}^{2+}$ .

Europium monoxide is relatively transparent in the visible and infrared spectral regions. In these regions it exhibits remarkably large magneto-optical effects arising from highly polarized europium  $4f^7$  to  $4f^6(5d)$  optical transitions.

Thin films of europium monoxide have been studied with regard to the possibility of using them in memory devices employing a thermo-magneto-optical recording principle. They are found to possess a sufficiently high read-out efficiency and a low point recording energy density so that they are suitable for use as a storage medium in a semiconductor laser reversible optical memory. There is an optimum film thickness for such application and this thickness depends on the thermal properties of the film and the substrate as well as on the optical properties.

Nonstoichiometric europium monoxide can be prepared with an oxygen-rich or oxygen-deficient composition. Oxygen-rich europium monoxide crystals are insulators and oxygen-deficient ones are extrinsic semiconductors (anion vacancies acting as donor centers).

A metal-semiconductor transition occurs in oxygen-deficient europium monoxide near 50 K. It has been suggested as the cause for this transition that at low temperatures the electrons are only very weakly bound to the oxygen vacancies and the electrical conduction is therefore metallic, but as the temperature is increased to near and above the transition temperature the electrons localized and form bound magnetic polarons by ordering the  $\text{Eu}^{2+}$  spins neighboring the vacancy, and therefore the electrical conduction becomes semiconducting.



The electrical resistivity of oxygen-deficient europium monoxide is very remarkable. As mentioned before the electrical conductivity is metallic below 50 K, at which temperature the electrical resistivity begins an enormous sharp increase (by more than 10 orders of magnitude in some samples) over a small temperature range of only about 20 degrees to reach a peak just above the Curie temperature where the resistivity starts to decrease gradually in a manner of that of an ordinary extrinsic semiconductor.

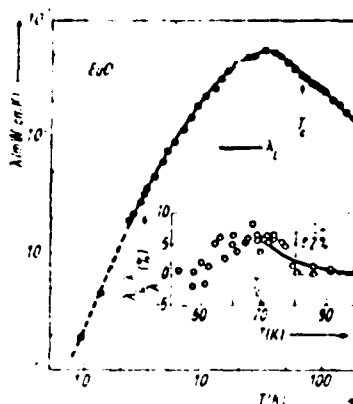
A systematic and exhaustive search of the world literature for the pertinent references on the thermophysical, electrical, and optical properties of europium monoxide has been conducted and the results are given in the following subsections. Typical data on each of the properties are also presented, if available.

#### a. Thermal Conductivity

The literature search uncovers the following references:

T037717	T046372	T051134	T059658	T074970
T046346	T047036	T053424	T069951	A000001

Typical data on the thermal conductivity of europium monoxide as taken from T069951 are shown below.



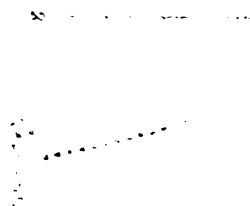
The points show the measured thermal conductivity of EuO. The two low temperature points were obtained in a separate experiment. The inset shows on a linear scale the pertinent difference between the measured and the model thermal conductivities in the vicinity of the Curie point.

### b. Specific Heat

The literature search uncovers the following references:

T040508	T058291	T073787	T080382	T084031	E018414
T047793	T069855	T074970	T080383	T085581	E038324
T052323	T071595	T075808	T080418	T085582	E039583
T052477	T073401	T077651	T083615	T089265	

Typical data on the specific heat of europium monoxide as taken from T077651 are shown below.

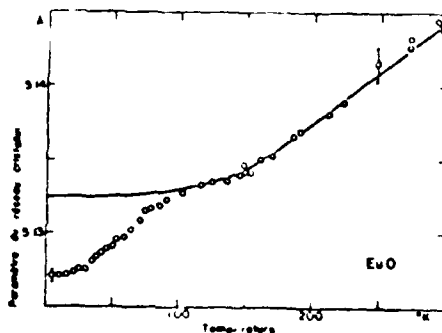


Specific heat of EuO (samples I and II) as a function of T.

### c. Thermal Linear Expansion

The literature search uncovers the following references: T043226 and T052700.

Typical data on the thermal linear expansion of europium monoxide as taken from T052700 are shown below.

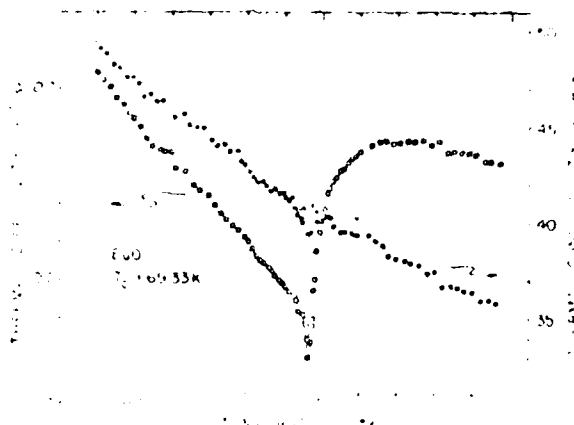


Thermal expansion of europium monoxide. The continuous curve represents the thermal expansion of a Debye solid with a characteristic temperature  $\theta = 410$  K.

#### d. Thermal Diffusivity

The literature search uncovers the following reference: T074970.

Typical data on the thermal diffusivity of europium monoxide as taken from T074970 are shown below.



Thermal diffusivity (squares) and thermal conductivity (circles) of EuO.

#### e. Thermal Emittance

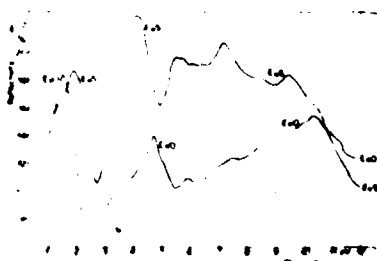
The literature search uncovers no reference on the thermal emittance.

#### f. Thermal Reflectance

The literature search uncovers the following references:

T053803	T054791	T058738	T068079	T071313	T075926	E046383	A000002
T053995	T055037	T062817	T070363	T073788	T080779	E080725	A000003

Typical data on the thermal reflectance of europium monoxide as taken from T070363 are shown below.



Reflectivity of EuO, EuS at 300 K.

### g. Thermal Absorptance

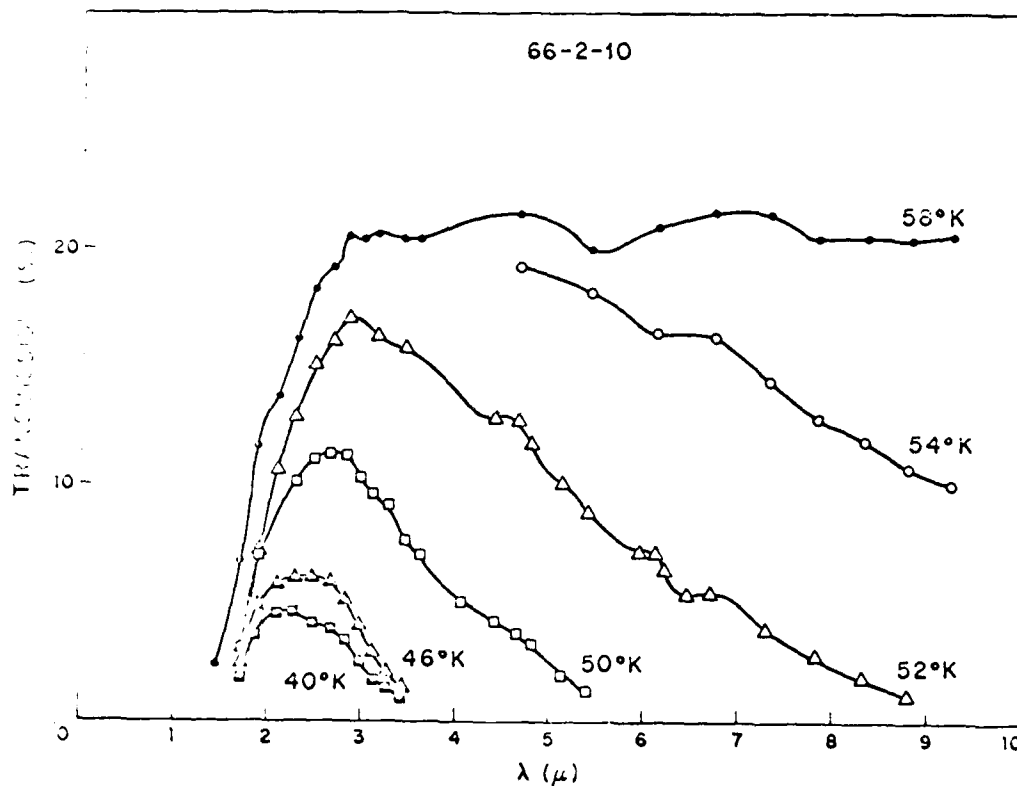
The literature search uncovers no reference on the thermal absorptance.

### h. Thermal Transmittance

The literature search uncovers the following references:

T050067    T061288    T064771    T071829    E047423    E078766    E106683

Typical data on the thermal transmittance of europium monoxide as taken from T064771 are shown below.



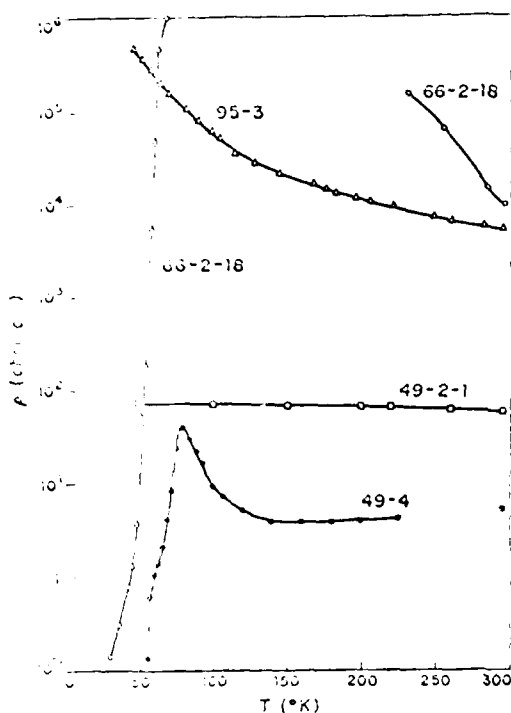
Transmission vs. wavelength for EuO sample 66-2-10. The measurements show the transition behavior which occurs near 50 K.

### i. Electrical Resistivity

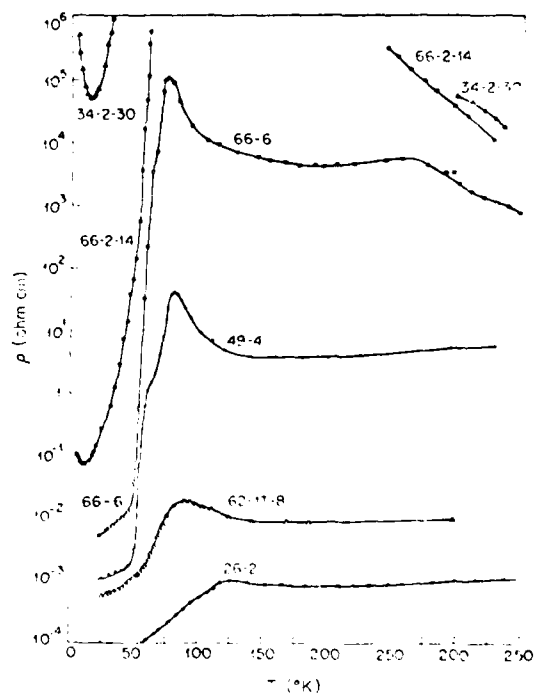
The literature search uncovers the following references:

T051134	E033026	E042831	E050887	E073494	E104938	A000008	A000015
T064771	E033163	E042856	E050888	E073943	E105465	A000009	A000016
T067524	E035354	E043549	E052969	E081120	E106738	A000010	A000017
T069722	E036806	E046381	E053158	E094722	A000004	A000011	A000018
E012228	E036859	E048092	E054573	E094771	A000005	A000012	
E024463	E037138	E049085	E060295	E096309	A000006	A000013	
E029645	E042679	E049301	E060440	E104930	E000007	A000014	

Typical data on the electrical resistivity of europium monoxide as taken from T064771 are shown below.



Four resistivity-vs-temperature curves for EuO. Curves for samples 66-2-18 and 49-4 represent type-A behavior; those of 95-3 and 49-2-1, type-B behavior. (Type-A: oxygen-deficient crystal; type-B: stoichiometric crystal.)



Resistivity vs temperature for representative type-A EuO samples showing change of behavior with increasing conductivity level.

#### j. Dielectric Constant

The literature search uncovers the following references:

T075926	E035354	E040275	E051185	E073535
E029645	E036598	E043549	E053052	E105465

Typical data on the dielectric constant of europium monoxide as taken from E105465 are shown below.

The dielectric constants of EuSe and EuO at the frequency 23 GHz.

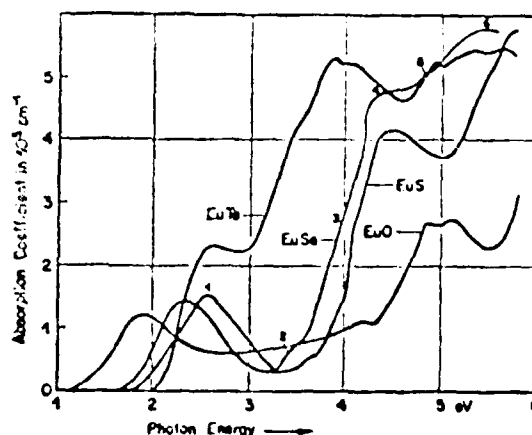
Sample	T/K	Volume/mm <sup>3</sup>	Dielectric Constant
EuSe(annealed)	293	0.302	12.1
EuSe (unannealed)	4.2	0.173	11.4
EuO	293	0.115	24.0

#### k. Absorption Coefficient

The literature search uncovers the following references:

T050067	T069722	E023252	E042799	E046391	E052969	E057182
T064771	T073788	E035802	E042848	E048048	E053052	E060259
T067524	T075926	E036859	E045104	E048527	E053158	E102340
T068016	E019959	E037259	E046390	E050888	E053358	A000018

Typical data on the absorption coefficient of europium monoxide as taken from E048048 are shown below.



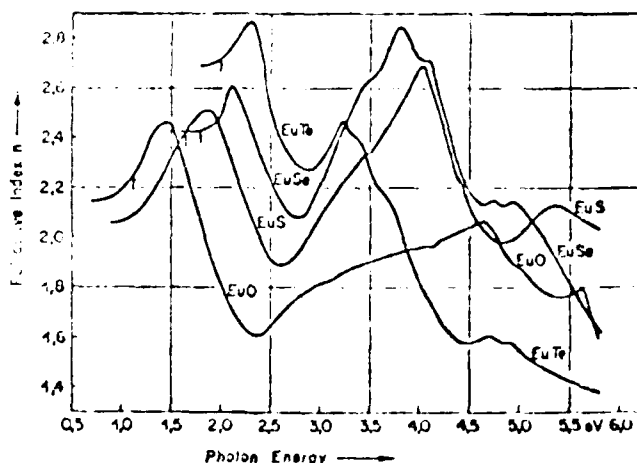
Absorption coefficient of the Eu-chalcogenides at 300 K.

#### l. Refractive Index

The literature search uncovers the following references:

E036598	E039161	E048048
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Typical data on the refractive index of europium monoxide as taken from E048048 are shown below.



Refractive index of the Eu-chalcogenides at 300 K.

### 2.9. Sodium Tungsten Bronze

Sodium tungsten bronzes ( $\text{Na}_x\text{WO}_3$ ) are nonstoichiometric compounds with  $x$  values in the range  $0 < x < 1$ . The crystal structure of the compounds has high symmetry for high  $x$  values and low symmetry for low  $x$  values. They have the cubic crystal structure of the perovskite type for  $0.2 < x < 1.0$  and the body-centered tetragonal crystal structure of  $x < 0.2$ ; however, it has also been reported that the cubic crystal structure extends only to  $x \approx 0.4$ .

The cubic sodium tungsten bronzes are metallic. Their colors vary from violet to gold with increasing  $x$ . Those compounds with high  $x$  values are excellent electrical conductors. At  $x = 0.75$ , the sodium atoms in the compound are partially ordered and the crystal has a superlattice structure. Anomalies in the variations of electrical resistivity, Hall coefficient, and other properties with sodium concentration  $x$  have been observed in the region of the superlattice structure.

As the sodium content is lowered, the electrical conductivity worsens. At a critical value of  $x \approx 0.2$ , a metal-insulator transition occurs. Compounds with  $x$  lower than the critical value become insulators and have the tetragonal crystal structure.

A second-order phase transition has been reported to exist in cubic metallic sodium tungsten bronzes. The transition temperature varies with the sodium concentration and has been determined by specific heat measurements

[T082706] as 435, 410, and 395 K respectively for bronzes with  $x = 0.794$ , 0.698, and 0.485. Anomalies in thermal, electrical, optical, and other properties have been observed near this phase transition.

A systematic and exhaustive search of the world literature for the pertinent references on the thermophysical, electrical, and optical properties of sodium tungsten bronzes has been conducted and the results are given in the following subsections. Typical data on each of the properties are also presented, if available.

#### a. Thermal Conductivity

The literature search uncovers the following references:

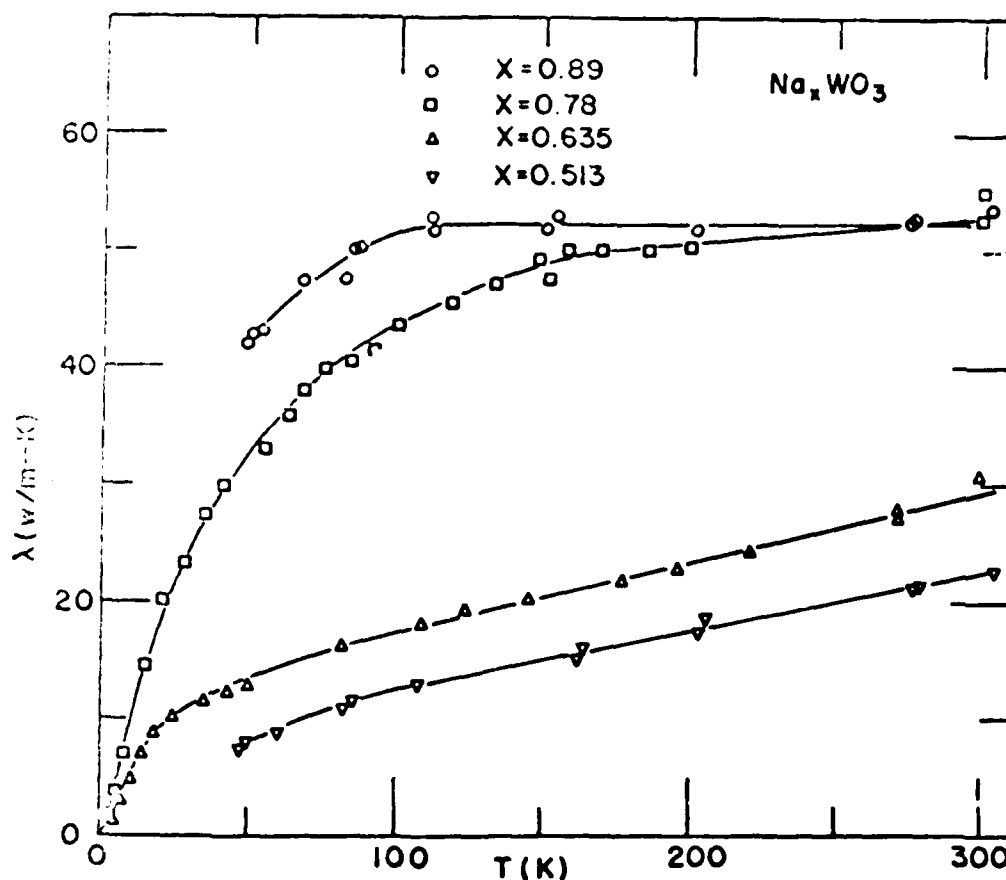
T037867

T056363

T057628

T064339

Typical data on the thermal conductivity of sodium tungsten bronzes as taken from T057628 are shown below.



The thermal conductivities versus temperature for the four bronzes.



## b. Specific Heat

The literature search uncovers the following references:

T006664    T008416    T038822    T073790    T081785    T082706    T086872

Typical data on the specific heat of sodium tungsten bronzes as taken from T082706 are shown below.

## Specific heat of tungsten bronzes

T (°C)	Cp (cal/mole CuO) (MW 143.1) (MW 247.8) (MW 412.811)			T (°C)	Cp (cal/mole CuO) (MW 143.1) (MW 247.8) (MW 412.811)		
	(MW 143.1)	(MW 247.8)	(MW 412.811)		(MW 143.1)	(MW 247.8)	(MW 412.811)
0	71.2	75.4	79.2	435	99.7	103.8	111.3
10	72.4	76.4	80.2	440	100.1	104.4	111.5
20	73.7	77.5	81.3	445	100.2	104.7	111.6
30	74.8	78.7	82.3	450	100.7	105.1	111.9
40	75.5	79.0	83.2	455	101.0	105.4	112.0
50	76.5	81.0	84.2	460	101.5	105.9	112.1
60	77.6	81.9	85.1	465	101.7	106.2	112.4
70	78.4	82.8	86.2	470	102.1	106.6	112.7
80	79.5	83.8	87.3	475	102.6	107.0	113.1
90	80.6	84.7	88.2	480	102.7	107.2	113.2
100	81.5	85.5	89.1	485	103.4	107.7	113.2
110	82.1	86.2	90.2	490	103.6	107.9	113.1
120	83.1	87.2	91.2	495	103.8	108.1	113.0
130	84.1	88.3	92.2	500	104.2	108.2	113.5
140	84.9	89.4	92.8	505	104.3	108.5	113.5
150	85.6	90.6	93.7	510	104.7	108.9	113.8
160	86.6	91.8	94.5	515	105.0	109.1	113.1
170	87.2	91.4	95.1	520	105.3	109.9	113.7
180	87.7	91.8	95.7	525	105.5	110.2	114.0
190	88.3	92.3	96.0	530	105.7	110.2	113.8
200	89.0	92.1	97.2	535	105.9	110.5	114.1
210	89.5	93.8	97.7	540	106.1	110.5	114.4
220	90.5	94.5	98.2	545	106.6	110.9	114.7
230	90.9	95.3	98.5	550	106.9	111.3	114.8
240	91.5	95.7	99.0	555	107.2	111.3	115.0
250	91.9	96.2	99.4	560	107.5	111.5	115.9
260	92.1	96.4	99.8	565	107.6	111.9	115.1
270	92.5	96.9	100.2	570	107.9	112.4	115.9
280	93.2	97.3	100.8	575	108.2	112.3	115.8
290	93.6	97.5	101.1	580	108.4	113.0	115.9
300	94.1	98.2	101.6	585	108.6	113.2	115.9
310	94.2	98.8	102.1	590	108.8	113.5	116.2
320	94.5	99.3	102.5	595	109.0	113.7	116.1
330	95.0	99.7	102.7	600	109.1	113.8	116.4
340	95.3	100.2	103.7	605	109.5	114.2	116.8
350	95.7	100.8	103.9	610	109.7	114.5	117.1
360	96.3	101.2	104.1	615	110.1	115.0	117.5
370	97.1	101.5	104.6	620	110.3	115.1	117.6
380	97.9	102.0	105.1	625	110.3	115.2	117.7
390	98.7	102.7	105.3	630	110.4	115.3	117.9
400	99.4	103.4	105.7	635	110.5	115.4	118.2
410	99.0	104.2	106.6	640	110.8	115.8	118.4
420	97.6	104.6	107.0	645	111.0	115.9	118.6
430	97.8	103.9	107.7	650	111.1	116.1	118.7
440	97.7	103.7	108.7	655	111.3	116.3	118.9
450	97.6	103.5	109.6	660	111.2	116.4	119.2
460	97.1	103.6	110.5	665	111.5	116.7	119.7
470				670	111.8	116.7	119.8
480				675	112.3	116.8	119.9



#### d. Thermal Diffusivity

The literature search uncovers no reference on the thermal diffusivity.

#### e. Thermal Emittance

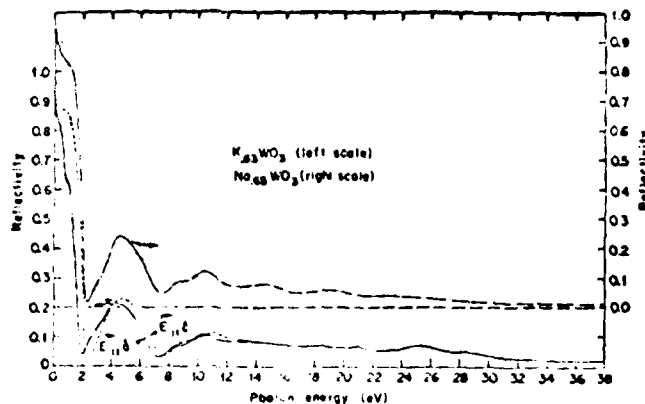
The literature search uncovers no reference data on thermal emittance.

#### f. Thermal Reflectance

The literature search uncovers the following references:

T058775	T067882	T078158	E078100
T060300	T072429	T090486	A000019

Typical data on the thermal reflectance of sodium tungsten bronze as taken from T072429 are shown below.

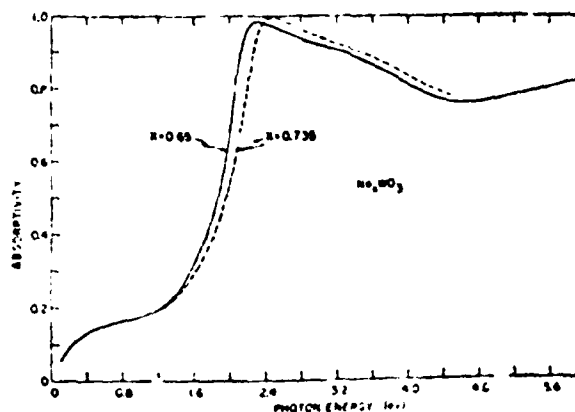


Reflectivity of cubic  $\text{Na}_{0.65}\text{WO}_3$  [(- ·) right scale] and tetragonal  $\text{K}_{0.63}\text{WO}_3$  at 300 K. (The data below 4.5 eV were taken at 4.2 K.)

#### g. Thermal Absorptance

The literature search uncovers the following references: T055710 and T072429.

Typical data on the thermal absorptance of sodium tungsten bronzes as taken from T072429 are shown below.



Absorptivity of two cubic sodium tungsten bronzes at 4.2 K.

#### h. Thermal Transmittance

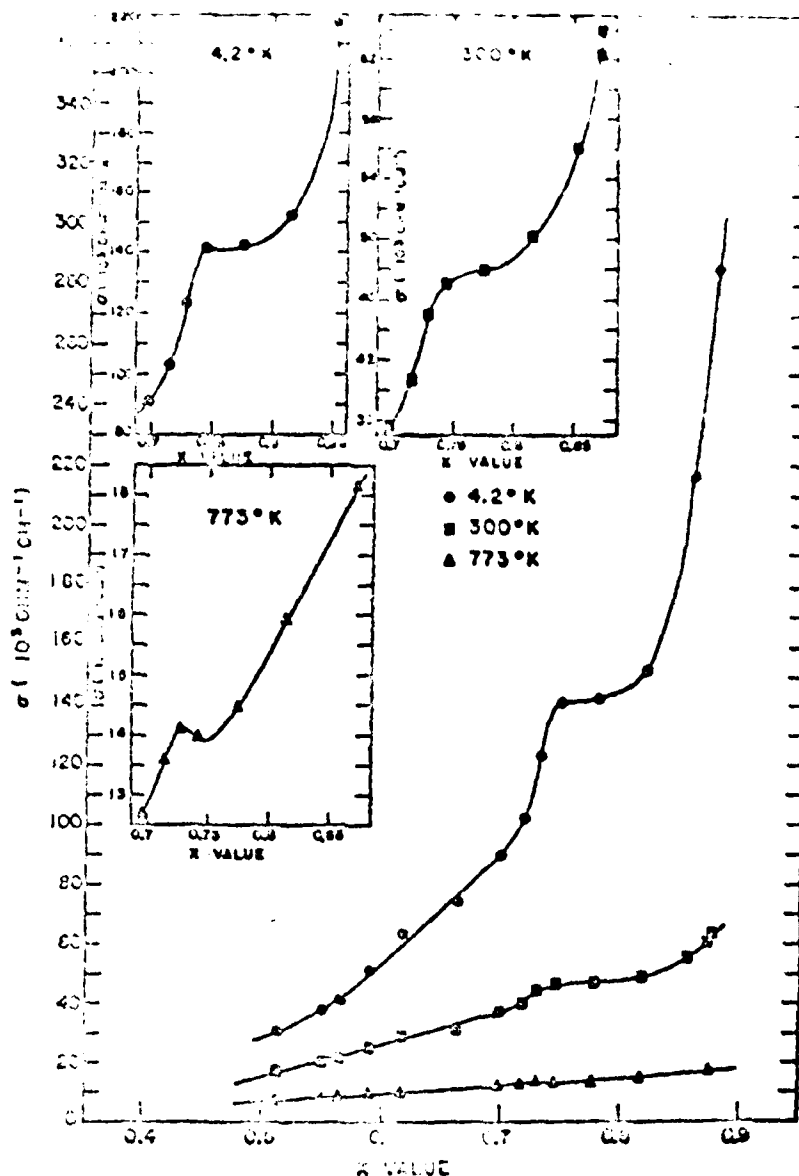
The literature search uncovers no reference on the thermal transmittance.

#### i. Electrical Resistivity

The literature search uncovers the following references:

T081785	E018378	E023056	E051858	A000022
T082219	E018519	E026083	E053013	A000023
E007235	E018975	E027642	E056765	A000024
E011045	E021138	E030029	A000020	A000025
E011046	E021140	E045096	A000021	A000026

Typical data on the electrical resistivity of sodium tungsten bronzes as taken from E030029 are shown below.

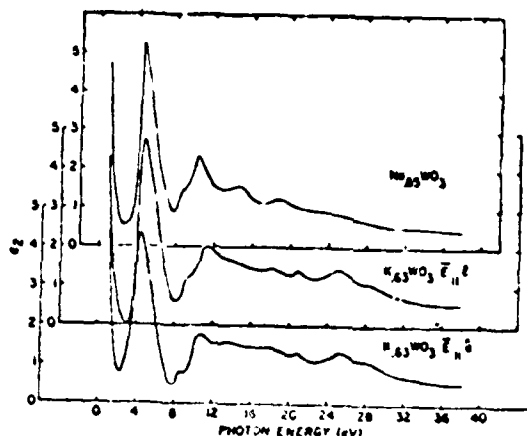


Conductivity of  $\text{Na}_x\text{WO}_3$  as a function of sodium concentration at 4.2, 300, and 773 K.

#### j. Dielectric Constant

The literature search uncovers the following references: T072429 and A000019.

Typical data on the dielectric constant of sodium tungsten bronze as taken from T072429 are shown below.

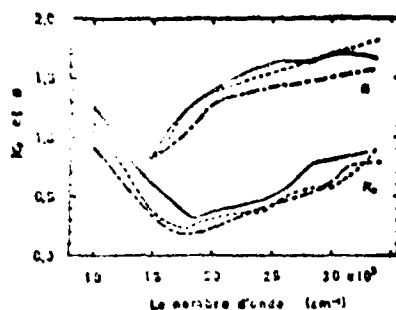


Imaginary part of the dielectric constant of cubic  $\text{Na}_{0.65}\text{WO}_3$  and tetragonal  $\text{K}_{0.63}\text{WO}_3$  derived from the data by Kramers-Kronig analysis.

#### k. Absorption Coefficient

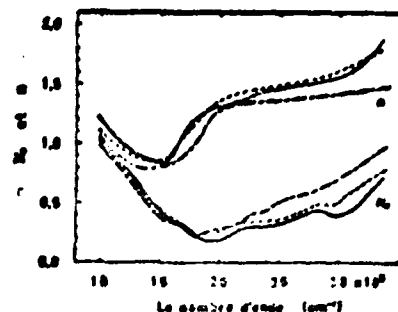
The literature search uncovers the following reference: T078158, which, however, is for sodium potassium tungsten bronzes.

Typical data on the absorption coefficient of sodium potassium tungsten bronzes as taken from T078158 are shown below.



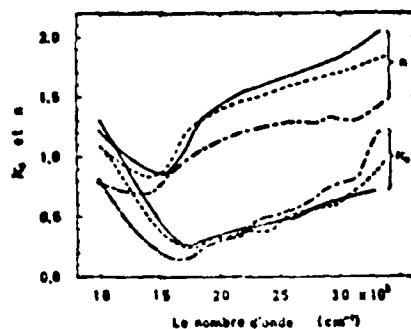
The absorption coefficient,  $K_0$ , and the refractive index,  $n$ , of:

- $\text{Na}_{0.43}\text{K}_{0.21}\text{WO}_3$
- - -  $\text{Na}_{0.42}\text{K}_{0.13}\text{WO}_3$
- · -  $\text{Na}_{0.43}\text{K}_{0.07}\text{WO}_3$



The absorption coefficient,  $K_0$ , and the refractive index,  $n$ , of:

- $\text{Na}_{0.30}\text{K}_{0.31}\text{WO}_3$
- - -  $\text{Na}_{0.22}\text{K}_{0.38}\text{WO}_3$
- · -  $\text{Na}_{0.10}\text{K}_{0.34}\text{WO}_3$



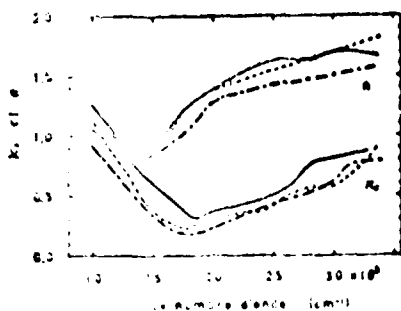
The absorption coefficient,  $K_0$ ,  
and the refractive index,  $n$ , of:

- $\text{Na}_{0.27}\text{K}_{0.23}\text{WO}_3$
- - -  $\text{Na}_{0.42}\text{K}_{0.13}\text{WO}_3$
- · -  $\text{Na}_{0.58}\text{K}_{0.10}\text{WO}_3$

#### 1. Refractive Index

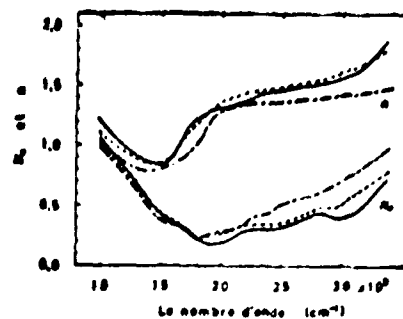
The literature search uncovers the following reference: T078158, which, however, is for sodium potassium tungsten bronzes.

Typical data on the refractive index of sodium potassium tungsten bronzes as taken from T078158 are shown below.



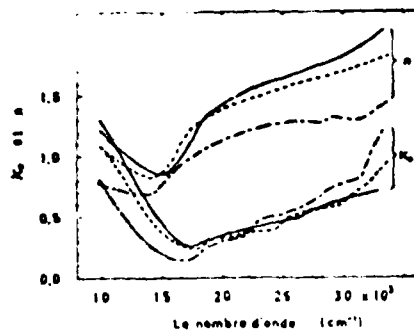
The absorption coefficient,  $K_0$ ,  
and the refractive index,  $n$ , of:

- $\text{Na}_{0.43}\text{K}_{0.21}\text{WO}_3$
- - -  $\text{Na}_{0.42}\text{K}_{0.13}\text{WO}_3$
- · -  $\text{Na}_{0.43}\text{K}_{0.07}\text{WO}_3$



The absorption coefficient,  $K_0$ ,  
and the refractive index,  $n$ , of:

- $\text{Na}_{0.30}\text{K}_{0.31}\text{WO}_3$
- - -  $\text{Na}_{0.22}\text{K}_{0.38}\text{WO}_3$
- · -  $\text{Na}_{0.10}\text{K}_{0.34}\text{WO}_3$



The absorption coefficient,  $K_0$ ,  
and the refractive index,  $n$ , of:

—  $\text{Na}_{0.27}\text{K}_{0.22}\text{WO}_3$   
 ---  $\text{Na}_{0.42}\text{K}_{0.13}\text{WO}_3$   
 - · -  $\text{Na}_{0.58}\text{K}_{0.10}\text{WO}_3$

## 2.10. Nickel Monosulfide

Nickel Monosulfide (NiS) is dimorphic and crystalizes in two crystal structures. The low-temperature form,  $\alpha$ -NiS, is rhombohedral of the millerite type, while the high-temperature form,  $\beta$ -NiS, is hexagonal of the NiAs type. The crystallographic transition temperature is 623 K. However, the transition from the high- to the low-temperature form is sluggish and the hexagonal form can easily be retained at room temperature. Single-phase  $\beta$ -NiS can be made to exist stably at room temperature by quenching it from above 623 K.

$\alpha$ -NiS is metallic with temperature-independent paramagnetism. It exists in nature as the mineral millerite which occurs usually in the form of capillary yellow crystals. Its melting point is about 1070 K and density is 5.3 to 5.7 g cm<sup>-3</sup>.

$\beta$ -NiS is metallic and paramagnetic at high temperature. Upon cooling it undergoes a first-order phase transition at a temperature around 260 to 280 K. This temperature varies with the sulfur content of each sample. Below the transition temperature  $\beta$ -NiS becomes semiconducting and antiferromagnetic. Some investigators have, however, reported that  $\beta$ -NiS is a semimetal instead of a semiconductor below the temperature of transition. Anomalies in thermal, electrical, magnetic, and other properties have been observed at this transition.

A systematic and exhaustive search of the world literature for the pertinent references on the thermophysical, electrical, and optical properties

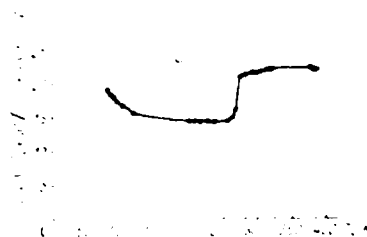


of nickel monosulfide has been conducted and the results are given in the following subsections. Typical data on each of the properties are also presented, if available.

#### a. Thermal Conductivity

The literature search uncovers the following reference: T067615.

Typical data on the thermal conductivity of nickel monosulfide as taken from T067615 are shown below.



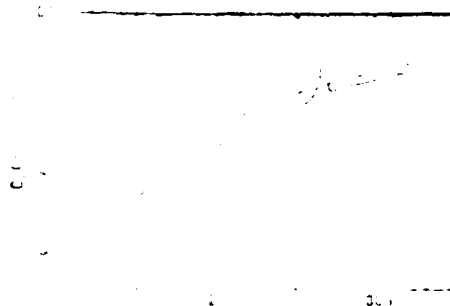
Temperature dependence of the thermal conductivity of  $\text{NiS}_{1.03}$ .

#### b. Specific Heat

The literature search uncovers the following references:

T000442	T037754	T076595	T085431
T022749	T066676	T076720	A000033

Typical data on the specific heat of nickel monosulfide as taken from T076595 are shown below.



Changes in thermodynamic parameters at the first-order transition in nickel sulfide.

	$T_1$	$\Delta T$	$\Delta S$	$\Delta H$
$\text{Ni}_{1.00}\text{S}$	500	10	5.0	10
$\text{Ni}_{0.98}\text{S}$	495	10	5.0	10
$\text{Ni}_{0.95}\text{S}$	490	10	5.0	10

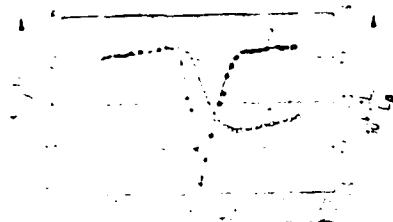
Heat capacity as a function of temperature for: solid line,  $\text{Ni}_{1.00}\text{S}$ ; dotted line,  $\text{Ni}_{0.98}\text{S}$ ; dashed line,  $\text{Ni}_{0.95}\text{S}$ . Data are obtained using 30-40-mg crystals and a heating rate of 10 K/min.

### c. Thermal Linear Expansion

The literature search uncovers the following references:

T071601      T072034      T079065

Typical data on the thermal linear expansion of nickel monosulfide as taken from T071601 are shown below.



Temperature dependence of (1)  $\Delta L/L_0$  and (2)  $\alpha$  for NiS.

### d. Thermal Diffusivity

The literature search uncovers no reference on the thermal diffusivity.

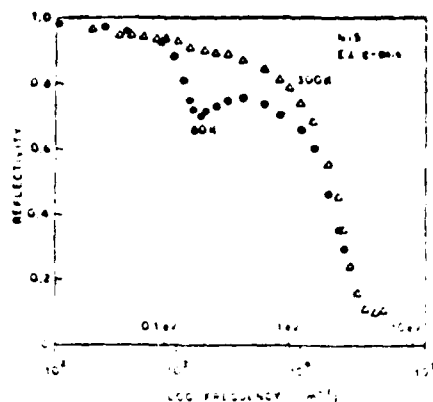
### e. Thermal Emittance

The literature search uncovers no reference on the thermal emittance.

### f. Thermal Reflectance

The literature search uncovers the following reference: T074708.

Typical data on the thermal reflectance of nickel monosulfide as taken from T074708 are shown below.



Polarized reflectivity spectra for a sample of NiS taken above and below the transition temperature  $T_t=230$  K. A prominent dip near 0.14 eV appears at low temperatures. There is also additional weak structure near 4.5 eV at both temperatures which is not shown here.

#### g. Thermal Absorptance

The literature search uncovers no reference on the thermal absorptance.

#### h. Thermal Transmittance

The literature search uncovers no reference on the thermal transmittance.

#### i. Electrical Resistivity

The literature search uncovers the following references:

T067615	E030946	E049296	E066700	E092795	A000034
T074708	E033485	E049621	E076569	E093734	A000035
E011896	E044059	E051017	E080574	E093757	A000036
E012182	E046461	E051115	E082564	E096635	A000037
E018179	E046831	E056164	E087204	E099152	
E024976	E048756	E064843	E087248	A000033	

Typical data on the electrical resistivity of nickel monosulfide as taken from T067615 are shown below.

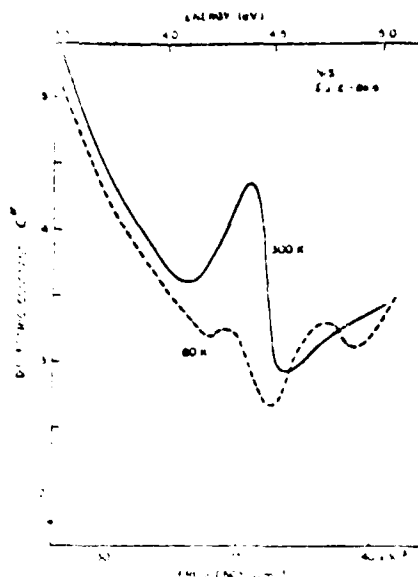


Electrical conductivity of  $\text{NiS}_{1.03}$ .

### j. Dielectric Constant

The literature search uncovers the following reference: T074708.

Typical data on the dielectric constant of nickel monosulfide as taken from T074708 are shown below.



Imaginary part of the dielectric constant  $\epsilon''$  obtained by Kramers-Kronig analysis of the reflectivity data in the visible and ultraviolet regions. The reflectivity data (not shown) have a spectral dependence of roughly the same form as  $\epsilon''$ . Note the reversion of the 300 K peak into two peaks separated by approximately 0.5 eV at 80 K.

### k. Absorption Coefficient

The literature search uncovers no reference on the absorption coefficient.

#### 1. Refractive Index

The literature search uncovers no reference on the refractive index.

#### 2.11. Nickel Disulfide

Nickel disulfide ( $\text{NiS}_2$ ) is a paramagnetic semiconductor or insulator (if pure and stoichiometric) with a cubic crystal structure of the pyrite type. It occurs in nature as the mineral vaesite with a density (determined by x-ray) of  $4.44 \text{ g cm}^{-3}$ . In the chemical process of separation of nickel as sulfide,

nickel disulfide is obtained as a crystalline, grayish black powder. On heating under atmospheric pressure nickel disulfide dissociates into nickel monosulfide and sulfur before reaching the melting point.

On cooling to a temperature around 40 K, a magnetic transition from a disordered paramagnetic to an ordered antiferromagnetic state occurs in nickel disulfide. A further transition to a weak ferromagnetic state at a still lower temperature below 30 K has also been reported.

A pressure-induced insulator-to-metal transition occurs in nickel disulfide under high pressure. The pressure of transition is about 32 kbar at room temperature and increases at high temperatures. This transition is not abrupt but stretches over a pressure range of about 8 kbar. It has been reported that a decrease in the volume of the crystal of about 0.4% occurs at the transition with no change in the crystal symmetry.

A systematic and exhaustive search of the world literature for the pertinent references on the thermophysical, electrical, and optical properties of nickel disulfide has been conducted and the results are given in the following subsections. Typical data on each of the properties are also presented, if available.

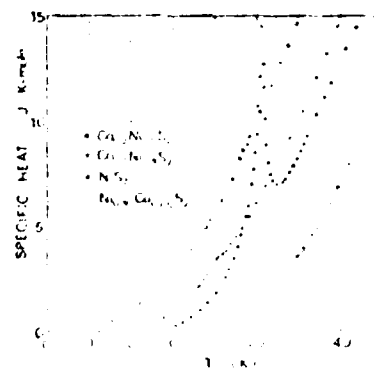
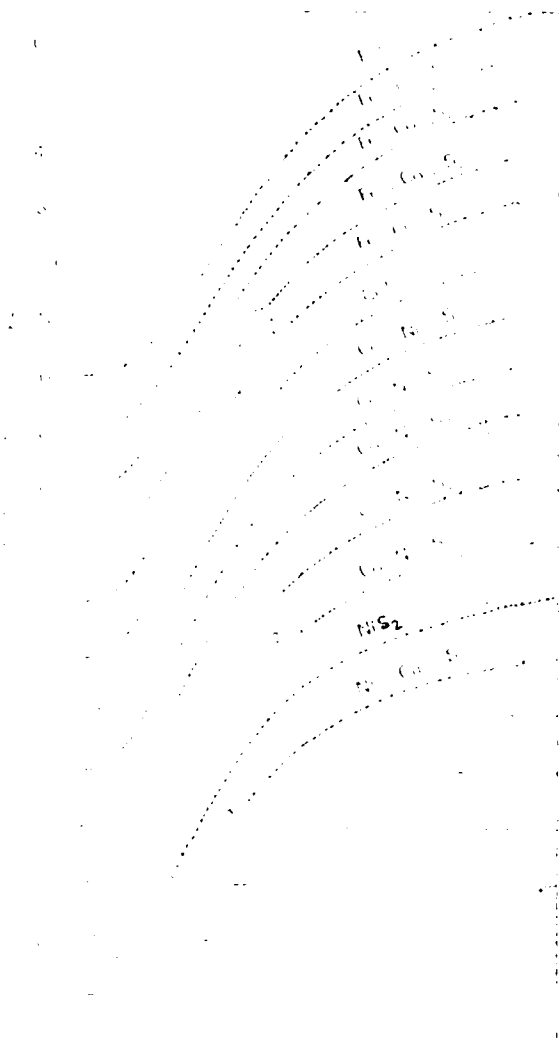
#### a. Thermal Conductivity

The literature search uncovers no reference on the thermal conductivity.

#### b. Specific Heat

The literature search uncovers the following references: T085903 and T088714.

Typical data on the specific heat of nickel disulfide as taken from T085903 are shown below.



Low temperature parts of the specific heats of weakly ferromagnetic compounds. Note that the abscissa is shifted 10 K each.

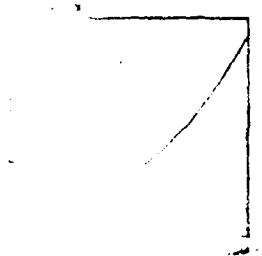
Specific heat of  $\text{FeS}_2\text{-CoS}_2\text{-NiS}_2\text{-Cu}_{0.05}\text{Ni}_{0.95}\text{S}_2$  solid solutions. Solid curves are computed ones for lattice and electronic contributions  $C_L + C_E$ .

#### c. Thermal Linear Expansion

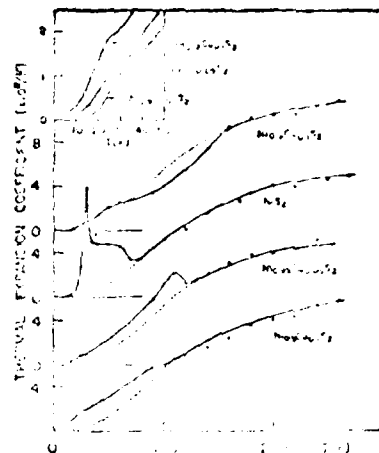
The literature search uncovers the following references:

T056221      T085237      T089396

Typical data on the thermal linear expansion of nickel disulfide as taken from T085237 are shown below.



Thermal expansion of  $\text{NiS}_2$ .



Coefficient of thermal expansion. Dashed line shows  $\alpha$  in paramagnetic state which is computed from  $\alpha$  above  $T_N$ . The insert shows the anomalies in  $\alpha$  associated with the appearance of weak ferromagnetism.

#### d. Thermal Diffusivity

The literature search uncovers no reference on the thermal diffusivity.

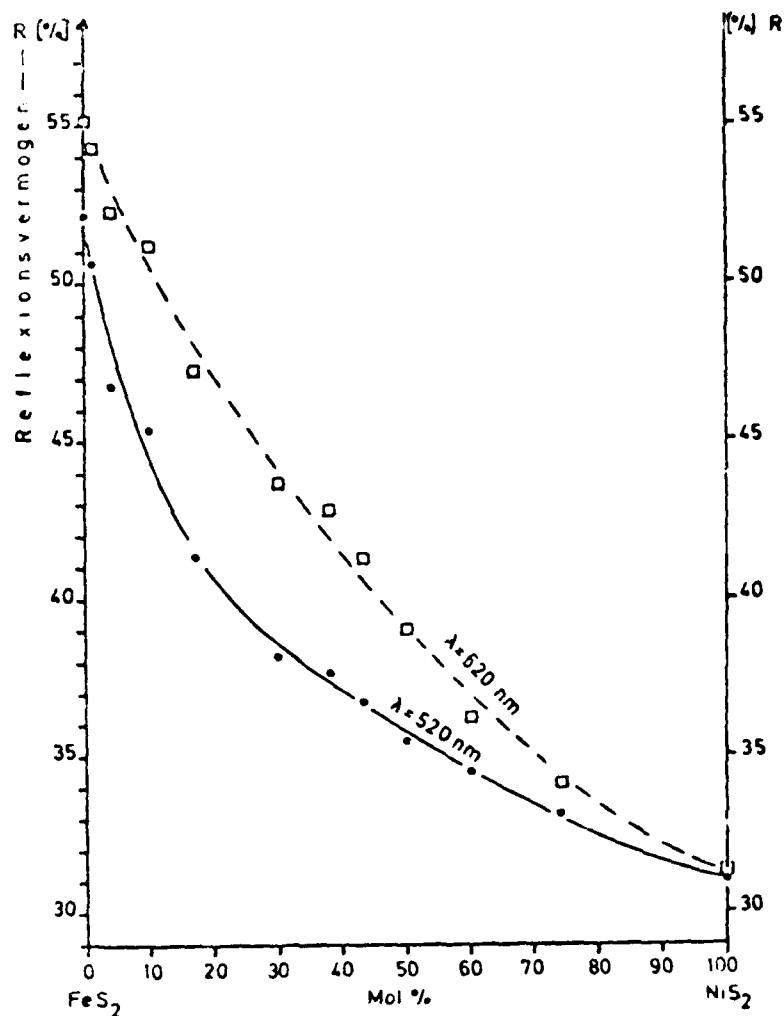
#### e. Thermal Emittance

The literature search uncovers no reference on the thermal emittance.

#### f. Thermal Reflectance

The literature search uncovers the following references: T055278 and T060195.

Typical data on the thermal reflectance of nickel disulfide as taken from T055278 are shown below.



The reflectance at  $\lambda = 520$  nm and  $\lambda = 620$  nm as a function of molar composition of  $\text{FeS}_2$ - $\text{NiS}_2$  mixed crystals ( $\text{CoS}_2$  concentration 1-2%).

#### g. Thermal Absorptance

The literature search uncovers no reference on the thermal absorptance.

#### h. Thermal Transmittance

The literature search uncovers no reference on the thermal transmittance.

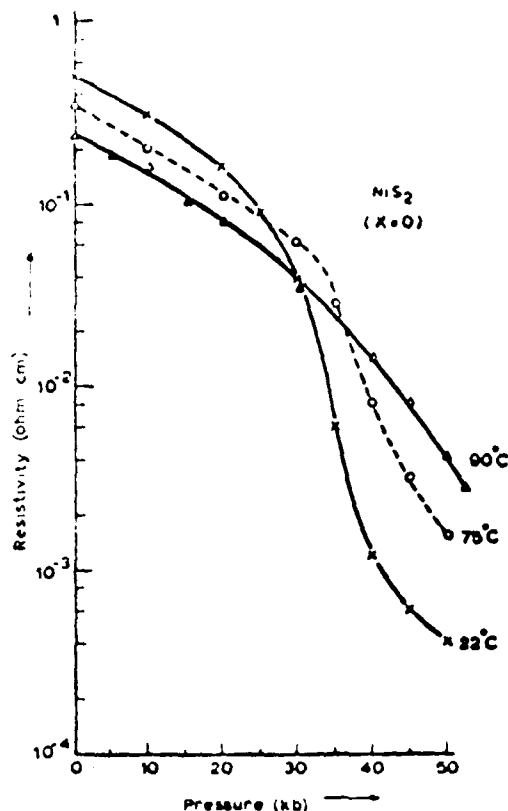
#### i. Electrical Resistivity

The literature search uncovers the following references:



T088714 E047263 E057669 E077333 E081927 E099326 E107374 A000039  
 E009475 E051115 E073435 E081191 E086262 E102516 A000038 A000040

Typical data on the electrical resistivity of nickel disulfide as taken from E047263 are shown below.



Variation of resistivity with pressure at different temperatures for single-crystal  $\text{NiS}_2$ . The transition at 22 °C occurs near 32 kb. At higher temperatures the transition occurs at higher pressures, and becomes less well-defined.

#### j. Dielectric Constant

The literature search uncovers no reference on the dielectric constant.

#### k. Absorption Coefficient

The literature search uncovers no reference on the absorption coefficient.

#### l. Refractive Index

The literature search uncovers no reference on the refractive index.

## 2.12. Samarium Monosulfide

Samarium monosulfide ( $\text{SmS}$ ) is a paramagnetic n-type semiconductor with an energy gap of 0.24 eV. It crystallizes in a face-centered cubic crystal structure of the NaCl type with a theoretical density of  $6.01 \text{ g cm}^{-3}$  and a melting point of about 2215 K.

All the monosulfides of rare-earth metals are metallic except those of samarium, europium, and ytterbium, which are nonmetallic. This is closely related to the fact that all the other rare-earth monosulfides are trivalent compounds but those of samarium, europium, and ytterbium are divalent compounds. Because of the enhanced stability of the dipositive states of samarium ( $\text{Sm}^{2+}$ ), europium ( $\text{Eu}^{2+}$ ), and ytterbium ( $\text{Yb}^{2+}$ ), the concentration of conduction electrons in their divalent monosulfides is depleted to such an extent that they become semiconductors or insulators. This fact has a direct bearing on the pressure-induced semiconductor-metal transition in samarium monosulfide discussed below.

At increasing pressure, samarium monosulfide undergoes a sharp transition from a semiconducting to a metallic state at a pressure of 6.5 kbar at room temperature with an accompanying large decrease in the atomic volume of the order of 20%. This semiconductor-metal transition is caused by the conversion under high pressure of the dipositive ions ( $\text{Sm}^{2+}$ ) to the smaller tripositive ions ( $\text{Sm}^{3+}$ ), thus rendering the change of samarium monosulfide from a divalent compound (semiconducting) to a trivalent compound (metallic). The metallic trivalent state is characterized by a golden yellow luster. At decreasing pressure, the transition pressure is about 0.8 kbar. Discontinuous changes in many physical properties of samarium monosulfide have been observed at this transition.

It has been reported that a thin layer on the surface of divalent semiconducting samarium monosulfide can be converted into the trivalent metallic state by means of internal or external stress, and small spots on this metallic surface can be reconverted back into the semiconducting state by short laser pulses [A000042]. Thin films of semiconducting samarium monosulfide can also be converted into the metallic state by means of internal stress such as that produced by surface polishing, and spots on such metallic thin films can also

be reconverted back into the semiconducting state by short laser pulses [T081396]. Application of such laser writing-reading on thin films of samarium monosulfide to the nonvolatile optical data storage has been suggested.

A systematic and exhaustive search of the world literature for the pertinent references on the thermophysical, electrical, and optical properties of samarium monosulfide has been conducted and the results are given in the following subsections. Typical data on each of the properties are also presented, if available.

#### a. Thermal Conductivity

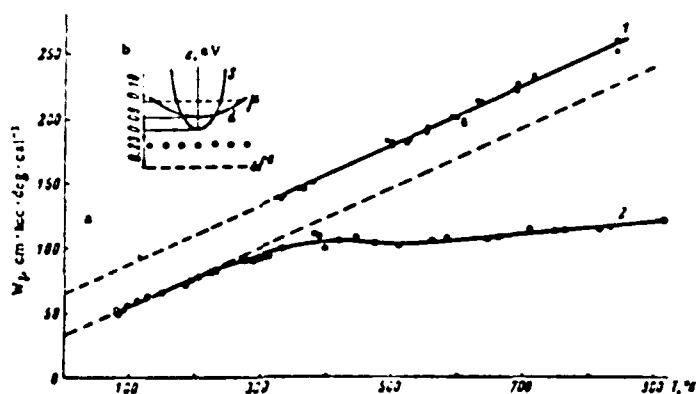
The literature search uncovers the following references:

T030066      T087584      E071576

Typical data on the thermal conductivity of samarium monosulfide as taken from T087584 are shown below.



Temperature dependence of the thermal conductivity of two SmS samples: (1) sample no. 1, (2) sample no. 2.



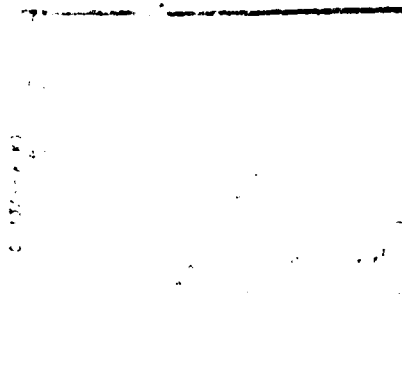
a) Temperature dependences of the thermal resistivity of the SmS lattice: 1) sample no. 1; 2) sample no. 2. b) Schematic representation of the conduction band of semiconducting SmS ( $m_s = 0.78 m_0$ ,  $m_d = 1.4 m_0$ ) at 500 K and the position of the Fermi level in the doped sample no. 2.

### b. Specific Heat

The literature search uncovers the following references:

T043957      T061497      T070639      T087591      T088277

Typical data on the specific heat of samarium monosulfide as taken from T070639 are shown below.



Heat capacity of SmS at approximately 15-kbar (triangles), and at zero pressure (circles).

### c. Thermal Linear Expansion

The literature search uncovers the following reference: T083829.

This document, however, does not report any numerical data but gives same qualitative information on the thermal linear expansion of samarium monosulfide, which is presented below.

An ionic model has been proposed which is capable of accounting for the temperature-induced valence transitions observed in the chemically collapsed Sm monochalcogenides. In addition, an expression has been deduced which enables the intermediate valence, corresponding to an extremum point on the volume-temperature curve, to be deduced (equation 20). This expression is largely insensitive to refinements of the basic model, depending primarily on the energy level structure of the Sm ions in their integral valence states ( $f^5$  and  $f^6$ ). The anomalous expansion (negative at low temperatures to positive at high temperatures) is largely a consequence of the ionic entropy terms in the free energy, the lattice vibrations giving a relatively small contribution. The thermal contraction at low temperature enables  $[(\partial p / \partial T)_V]$  to become very small, eventually giving rise to a first-order (or sharp second-order) transition via the same mechanism that drives the corresponding pressure induced transition in pure SmS. The positive expansion at high temperatures again makes  $[(\partial p / \partial T)_V]$  small, resulting in anomalously large thermal expansion, though now there is no singularity since  $T > T_c$ .

These conclusions will probably be applicable to other rare earth monochalcogenides under chemical pressure, although the phase transitions are expected to be less sharp.

#### d. Thermal Diffusivity

The literature search uncovers no reference on the thermal diffusivity.

#### e. Thermal Emittance

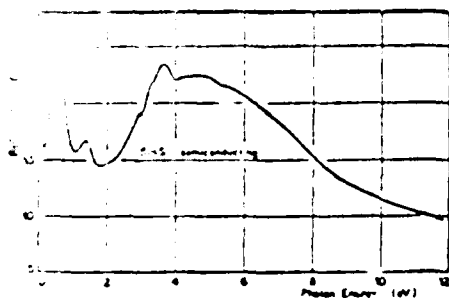
The literature search uncovers no reference on the thermal emittance.

#### f. Thermal Reflectance

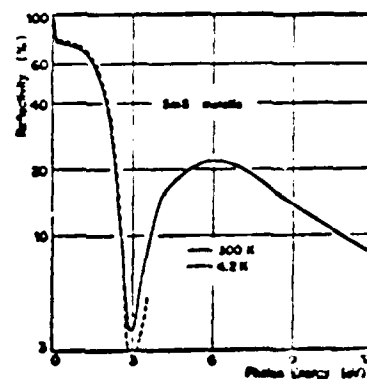
The literature search uncovers the following references:

T063258	T077034	T082161	T087820	A000041	A000044
T067832	T080393	T086126	T088206	A000042	A000045
T068556	T081396	T086127	T089892	A000043	

Typical data on the thermal reflectance of samarium monosulfide as taken from T088206 are shown below.



Reflectivity of semiconducting SmS.



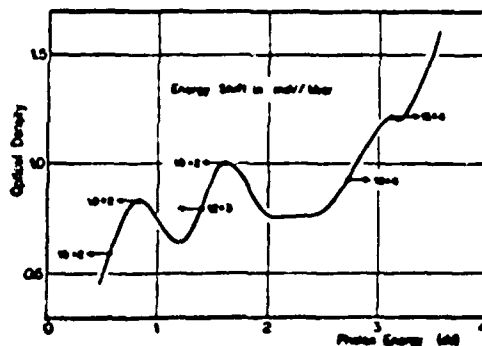
Reflectivity of metallic SmS.

#### g. Thermal Absorptance

The literature search uncovers the following references:

T084296	T087736	T088206	A000045	A000046	A000047
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Typical data on the thermal absorptance of samarium monosulfide as taken from T088206 are shown below.



Optical density of a semiconducting SmS film.

#### h. Thermal Transmittance

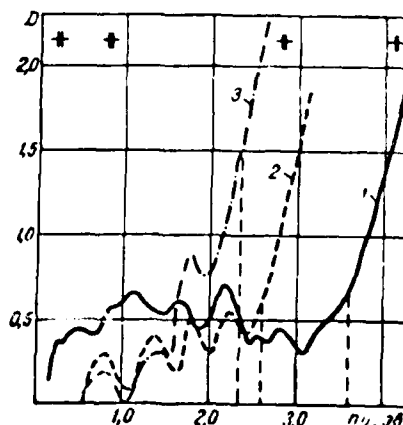
The literature search uncovers the following references:

T063258

T081396

T089892

Typical data on the thermal transmittance of samarium monosulfide as taken from T063258 are shown below.



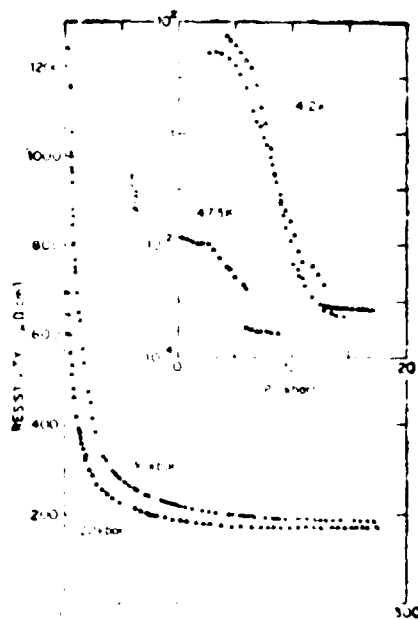
Spectra of transmission of films of SmS(1), SmSe(2), and SmTe(3).

#### 1. Electrical Resistivity

The literature search uncovers the following references:

T070639	T089953	E071576	E106953	A000055	A000063
T081079	T090081	E085576	A000048	A000056	A000064
T082161	E016920	E088286	A000049	A000057	A000065
T083643	E022419	E093158	A000050	A000058	
T086127	E033399	E100388	A000051	A000059	
T087584	E044959	E103680	A000052	A000060	
T088698	E046392	E105267	A000053	A000061	
T089693	E057706	E105281	A000054	A000062	

Typical data on the electrical resistivity of samarium monosulfide as taken from T070639 are shown below.

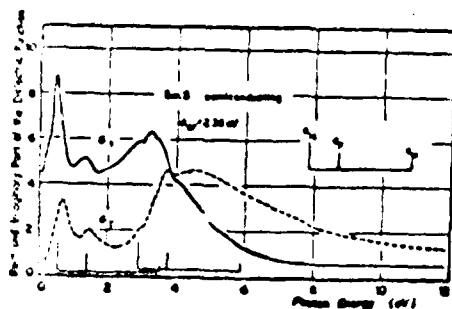


The resistivity vs temperature of SmS at 10 and 20 kbar. The inset compares the insulator-metal transition as a function of pressure at 4.2 and 473 K. The pressure transmitting medium was AgCl (circles), frozen (triangles) or liquid (squares) n-pentane isoamyl alcohol.

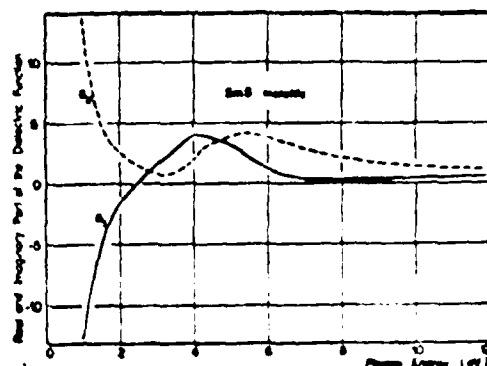
#### j. Dielectric Constant

The literature search uncovers the following reference: T088206.

Typical data on the dielectric constant of samarium monosulfide as taken from T088206 are shown below.



Dielectric function of semiconducting SmS.



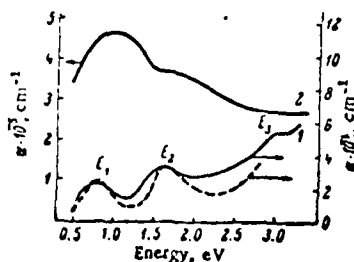
Dielectric function of metallic SmS.

#### k. Absorption Coefficient

The literature search uncovers the following references:

T068556    T068914    T083643    T084296    T087736    T088206    T089892

Typical data on the absorption coefficient of samarium monosulfide as taken from T087736 are shown below.



Absorption spectra of the semiconducting (curve 1, right-hand scale) and metallic (curve 2, left-hand scale) phases of SmS.

#### 1. Refractive Index

The literature search uncovers no reference on the refractive index.



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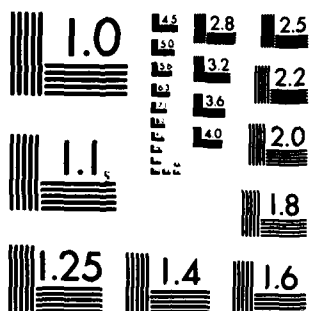
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